



Characterisation and Treatment of Nano-sized Particles, Colloids and Associated Polycyclic Aromatic Hydrocarbons in Stormwater

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Characterisation and Treatment of Nano-sized Particles, Colloids and Associated Polycyclic Aromatic Hydrocarbons in Stormwater



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Characterisation and Treatment of Nano-sized Particles, Colloids and Associated Polycyclic Aromatic Hydrocarbons in Stormwater

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PhD Thesis
June 2015

DTU Environment
Department of Environmental Engineering
Technical University of Denmark

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Associated Polycyclic Aromatic Hydrocarbons in Stormwater**

PhD Thesis, June 2015

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Preface

This PhD thesis presents the outcome of a project conducted in collaboration between the Department of Environmental Engineering, Technical University of Denmark (DTU) and the Department of Civil and Environmental Engineering, Chalmers University of Technology, Gothenburg, Sweden, in the period of December 2011 to May 2015. The majority of the experiments were conducted at DTU. A 3-month stay at Chalmers gave me the opportunity to work with new experimental methods. The project was founded by the Nordic Five Tech alliance (N5T) as a DTU scholarship. The project was supervised by Associate Professor Eva Eriksson as the main supervisor, and co-supervised by Associate Professor Ann-Margret Strömvall and Professor Anders Baun.

The thesis is organised in two parts: the first part puts the findings of the PhD into context in an introductory review; the second part consists of the papers listed below. These will be referred to in the text by their paper number written with the Roman numerals **I–V**.

- I.** Nielsen K., Mørch-Madsen A., Baun A. and Eriksson E. Characterisation and stability of humic acid and iron nano-sized colloids intended for simulated stormwater experiments (*Submitted*).
- II.** Nielsen K., Mikkelsen P. S., Sebastian C. and Eriksson E. Physical and chemical characterisation of stormwater particles (< 50 µm) and associated metals and polycyclic aromatic hydrocarbons (*Manuscript*).
- III.** Nielsen K., Mørch-Madsen A., Mikkelsen P. S., Eriksson E.. Effect of Disc Filtration with and without Addition of Flocculent on Nano- and Micro-Particles and Their Associated Polycyclic Aromatic Hydrocarbons in Stormwater. *Water*, 2015, 7, 1306–132
- IV.** Nielsen K., Mayer P., Eriksson E. Co-transport of PAHs by Particulate Matter, Colloids and Nano-sized Particles - using Analytical Passive Dosing to Determine the Enhanced Capacity of Stormwater (*Manuscript*).
- V.** Nielsen K., Kalmykova Y., Strömvall A-M., Baun A., Eriksson E. Particle Phase Distribution of Polycyclic Aromatic Hydrocarbons in Stormwater – Using Humic Acid and Iron Nano-sized Colloids as Test Particles. *Science of the Total Environment* *Science of the Total Environment*, 2015, 532, 103–111

In this online version of the thesis, paper **I-V** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from DTU Environment, Technical University of Denmark, Miljøvej, Building 113, 2800 Kgs. Lyngby, Denmark, info@env.dtu.dk

In addition, the following publications, not included in this thesis, were also concluded during this PhD study:

Sørud M., Nielsen K., Damskier S. S., Jørgensen A. T., Petersen M. F., Rasmussen L. K., Mikkelsen P. S., Eriksson E. (2013) DEMFIL – treatment of stormwater for recreational use. In proceedings (oral presentation, not attending). NORDIWA 2013: 13th Nordic Wastewater Conference, October 8–10, Malmö, Sweden.

Nørlem M., Petersen M. F., Mørch-Madsen A., Mikkelsen P. S., Eriksson E., Nielsen K., Rasmussen L. K. (2014) Demonstrationsanlæg for Filtrering af vejvand for udledning til ferskvandsområde: Afrapportering for projekt støttet af VTU - Fonden.

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I would also like to thank all of my co-authors for their collaboration during the publishing of our papers.

I would like to thank all of my colleagues at DTU Environment for making my work interesting, fun, and more than just a normal working day. I have had some great office mates who have been there when work has been difficult, but have also been there when it was time for celebration — for this I am forever grateful.

I would like to thank Dr. Mohammed Baalousha, Assistant Professor at the Center for Environmental NanoScience and Risk, University of South Carolina, USA, for his collaboration on Transmission Electron Microscope (TEM) pictures of particles in stormwater.

I would also like to thank Dr. Christian Engelbrekt, Postdoc at the Department of Chemistry, Technical University of Denmark, for his assistance with measurements on the NanoSight instrument. Likewise, I would like to thank Laboratory Technician Larisa Seerup, Department of Energy Conversion and Storage, for assistance on measurements on the Laser Particle Sizer.

During my 3-month stay at Chalmers (Sweden), I met new colleagues and friends who all took good care of me and made me feel at home. Thanks to all of you for making my stay a special time. I would especially like to thank Research Engineer Mona Pålsson for her assistance in the lab. I would like to thank the Otto Mønsted Foundation for help with the financing of the stay.

Finally, I would like to thank my family and friends for putting up with me during stressed times and supporting me through this journey.

“The only man who never makes a mistake is the man who never does anything.”

Theodore Roosevelt, 1900

Summary

Stormwater from urban areas contains a vast array of different pollutants, including particulate matter and organic and inorganic compounds as well as microbial pollution. These compounds can be found associated with particulate matter, colloids and nano-sized particles in stormwater. The associated pollutants will, if not removed in stormwater treatment facilities, be discharged into receiving surface waters, due to enhanced transportation exerted by the colloids and nano-sized particles. More stormwater than previously is separated from wastewater and drained to stormwater treatment facilities in Denmark. This is a consequence of climate changes, with increasing precipitation in Europe. The increased precipitation causes problems with hydraulic overloading of sewer systems and therefore stormwater is directed into stormwater drainage systems and to stormwater treatment facilities.

Since little is known about the colloids and nano-sized particle-enhanced transportation of pollutants in stormwater, it has been difficult to determine their quantitative role in the total release of pollutants into receiving waters. Therefore the main purpose of this thesis has been to document the presence and size distribution of colloids and nano-sized particles in stormwater, as well as quantify the particle-enhanced transportation of polycyclic aromatic hydrocarbons (PAHs) in stormwater.

Stormwater from five sites in Europe was collected to characterise the particulate matter, colloids and nano-sized particles in the stormwater, in terms of particle size distribution (PSD) and zeta potential. In combination with the characterisation of the particles, concentrations of organic and inorganic compounds were quantified in the stormwater, with a focus on PAHs, together with physical and chemical parameters such as pH, Total Suspended Solid (TSS), turbidity, and electrical conductivity.

The five sites where stormwater was sampled from used two different methods of stormwater treatment: settling and filtration, and four different treatment techniques: detention ponds, stormwater pond, disc filter and combined sedimentation tanks. From all sites, inlet and outlet stormwater were collected, and pollutant concentrations were quantified as well as the removal efficiencies calculated. The colloidal and nano-sized particle-enhanced transportation of pollutants was also scrutinised in the stormwater.

The μm -range PSD measured in the stormwater showed that the majority of the particles were $< 10 \mu\text{m}$ in diameter (both inlet and outlet samples). The nm-range PSD on the colloids and nano-sized particles was found in the size range of 50–200 nm in diameter. The zeta potentials were negative for all of the stormwater (-13 – -50 mV), indicating a negative surface charge. This indicates that the particles in the stormwater were of clay and silt and also humic and fulvic acids.

For all five stormwater treatment facilities, the measurements showed a reduction of particulate matter, quantified as TSS and turbidity, as well as organic and inorganic pollutant content from the inlet to the outlet samples. The PSD was found to be identical for inlet and outlet samples, despite a reduction in pollutant components. Sorption experiments using stormwater and a passive dosing technique revealed that the stormwater particulate fractions were able to sorb PAHs, thereby enhancing the transportation in stormwater.

In the stormwater collected from the four of the five different sites PAHs were found associated with the particulate fraction containing the large particles ($> 0.7 \mu\text{m}$). The PAHs were also found sorbed to the colloids (4.2-56%) and occurred in the dissolved fraction (0.9-25%). From one of the sites, 82% of the PAHs were found in the particulate fraction in the inlet sample and 18% in the colloidal fraction ($< 0.7 \mu\text{m}$). The PAHs occurred also in both fractions in the outlet samples, but in lower concentrations. Overall, it was found that 30–40% of the PAHs were associated with colloids ($< 0.7 \mu\text{m}$), and that the PAHs of 4–5 aromatic rings were more often in association with the colloid and nano-sized particles than with particles $> 10 \mu\text{m}$.

The particulate matter, colloids and nano-sized particles are able to sorb PAHs and thereby enhance the transportation of PAHs in stormwater systems. To gain a better understanding of the colloids and nano-sized particles in stormwater, techniques to separate nano-sized particles and colloids should be further investigated. Thereby a more quantitative measurement of the PSD could be achieved.

Dansk sammenfatning

Afstømmet regnvand fra byområder indeholder forurening i form af partikler organiske og uorganiske stoffer. Disse stoffer kan findes bundet til partikler, kolloider og partikler i nano-størrelse. De bundne stoffer vil, hvis ikke fjernet gennem rensning, blive udledt til overfladevand på grund af den forøgede transport sammen med partiklerne. Mængden af afstrømmet regnvand, der er separeret fra fælleskloak-systemet og ledt til regnvandsrensningssystemer er øget igennem tiden. Dette er b.l.a. en konsekvens af klimaændringer med en øget mængdenedbør over Europa. Den øgede nedbør har medført problemer med hydraulisk overbelastning af kloaksystemer og derfor bliver afstrømmet regnvand ledt til separate kloaker og videre til regnvands opsamlingsystemer.

Kun sparsom litteratur om øget transport af stoffer sorberet på kolloider og partikler i nano-størrelse i afstrømmet regnvand tilgængelig. Derfor er det vanskeligt at bestemme deres bidrag til forøgede transport af forurenende stoffer i afstrømmet regnvand. Hovedformålet med denne afhandling har været at dokumentere tilstedeværelsen og størrelsesfordelingen af kolloider og partikler i nano-størrelse i afstrømmet regnvand, samt at kvantificere den forøgede transport af polycykliske aromatiske kulbrinter (PAH'er) i afstrømmet regnvand.

Afstrømmet regnvand fra fem lokaliteter i Europa blev indsamlet til karakteriseringen af partikler, kolloider og partikler i nano-størrelse i afstrømmet regnvand, i form af partikelstørrelsesfordeling og zeta-potentiale. I kombination med karakterisering af partiklerne, blev koncentrationerne af organiske og uorganiske forbindelser målt i det afstrømmede regnvand, med fokus på PAH'er samt fysiske og kemiske parametre som pH, Total Suspended Solid (TSS), turbiditet og elektrisk ledningsevne.

De fem lokaliteter hvorfra afstrømmet regnvand blev indsamlet, anvender to forskellige metoder til regnvandsbehandling: bundfældning og filtrering. På de fem lokaliteter blev tre forskellige regnvandsbehandlingsteknikker brugt, regnvandsbassin, diskfilter og serieforbundet bundfældningstanke. Fra alle lokaliteter blev der indsamlet indløbs- og udløbs-prøver for at kunne bestemme fjernelseseffektiviteten i de forskellige metoder og derved bedømme den forøgede transport af forurenende stoffer i afstrømmet regnvand.

Partikelstørrelsefordelinger målt i afstrømmet regnvand viste, at hovedparten af partiklerne havde en partikel størrelsefordeling på $<10\text{ }\mu\text{m}$ i diameter, set både i indløbet og udløbet. Kolloiderne og partikler i nano-størrelse viste sig at være i størrelsesordenen 50–200 nm i diameter. Transmission Elektron Mikroskop billeder bekræftede de målte størrelser af kolloider og partikler i nano-størrelse.

Alle de undersøgte afstrømmede regnvands anlæg viste reduktion i TSS, turbiditet og organiske og uorganiske forurenende stoffer, selv om PSD viste sig at være den samme for indløbs- og udløbs -prøverne. Sorptions forsøg med afstrømmet regnvand og passiv dosseingsteknik viste at både partikler $>10\text{ }\mu\text{m}$, kolloider og nano-partikler var i stand til at binde PAH'er og dermed øge stoftransporten i regnvand.

Polycykliske aromatiske kulbrinter blev fundet i forbindelse med partikler og kolloider i regnvand. Fra en af lokaliteterne blev det målt at 82% af PAH'er blev fundet i den partikulære fraktion (partikler $>0.7\text{ }\mu\text{m}$) i indløbet og 18% blev fundet i fraktionen indeholdende partikler og kolloider ($<0.7\text{ }\mu\text{m}$). For udløbsprøver blev PAH'er også målt i begge fraktioner.

Overordnet set var 30–40% af PAH'erne i kombination med kolloider og nano-størrelse partikler ($<0.7\text{ }\mu\text{m}$), og de 4–5 ringede PAH'er blev oftere fundet i forbindelse med kolloider og partikler i nano-størrelse end det var tilfældet for partikler $>1\text{ }\mu\text{m}$.

Resultaterne af denne ph.d.-afhandling viser, at kolloider og partikler i nano-størrelse findes i afstrømmet regnvand, og at de kan være med til at forøge transporten af PAH'er. Partikelstørrelsefordelingsmålinger af kolloider og partikler i nano-størrelse i afstrømmet regnvand kan foretages med visse forbehold. Hvis der skal opnås en bedre forståelse for kolloider og nano-størrelse partiklers størrelser i afstrømmet regnvand skal en adskillelse af partiklerne opnås før mere kvantitative størrelsesmålinger kan opnås.

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Abbreviations

Ace	Acenaphthene
Acy	Acenaphthylene
Ant	Anthracene
BaAnt	Benzo[a]anthracene
BaPyr	Benzo[a]pyrene
BbFlu	Benzo[b]fluoranthene
BghiPer	Benzo[ghi]perylene
BkFlu	Benzo[k]fluoranthene
BOD	Biological Oxygen Demand
Chy	Chrysene
DiAnt	Dibenzo[a,h]anthracene
DLS	Dynamic Light Scattering
EC	Electrical Conductivity
EEA	European Environmental Agency
ERP	Electrical Resistive Pulse
EQS	Environmental Quality Standards
EU	European Union
Fe-n	Nano-sized iron(III)
Flt	Fluoranthene
Flu	Fluorene
HRT	Hydraulic retention time
HA-n	Nano-sized humic acid
HMW	High-molecular weight
LAR	Lokal Afledet Regnvand
LID	Low Impact Development
LLE	Liquid–Liquid extraction
Log K _{ow}	Octanol–water partitioning constant
LMW	Low-molecular weight
MMW	Medium-molecular weight
NAP	Naphthalene
nm	Nanometre (10 ⁻⁹)
NVOC	Non-Volatile Organic Carbon
NPDES	National Pollution Discharge Elimination System
PAHs	Polycyclic Aromatic Hydrocarbons
Phe	Phenanthrene
PSD	Particle Size Distribution
Pyr	Pyrene

SPE	Solid Phase Extraction
TEM	Transmission Electron Microscope
TSS	Total Suspended Solid
US-EPA	United States of America Environment Protection Agency
WFD	Water Framework Directive
WWTP	Waste Water Treatment Plant

1 Introduction

During the last 20 years, interest in stormwater quality has increased. Reasons for this include requests to use stormwater for gardening purposes or in households, and an environmental concern for discharging untreated stormwater directly into lakes, rivers and the sea. From a water utility point of view, a highly attractive form of separating stormwater from wastewater is to construct separate storm sewer systems in publically owned areas, e.g. roads (Malamataris 2014).

Climate changes with increased precipitation and, more frequently, heavy rain events have caused flooding's of streets and buildings around the world. The annual average precipitation in Northern and Central Europe has increased during the last century as a consequence of climate change (Hartmann et al. 2013). With an expected increase in daily precipitation, and especially more heavy rain events, overloading the combined sewers will increase in the future, yielding combined sewer overflow and creating a bigger need for separating stormwater from wastewater (Fowler et al. 1995).

Separating stormwater from wastewater became a national interest in Denmark after 2nd July 2011, when a cloudburst hit the Copenhagen area with 30–90 mm of rain during 24 hours and with a maximum intensity of 3.1 mm/min over two minutes in the most affected sites (Vejen 2011). The damage caused by combined sewer overflow and the flooding of roads and buildings, as well as health effects, was estimated at 0.64 billion euros (Johannsdottir et al. 2014). This major cloudburst, combined with smaller cloudbursts in the years before and after, together with daily problems with hydraulic overloading of combined sewers, has had intensive media coverage, whereby increasing the public awareness of separating stormwater from wastewater and the combined sewer system (Ingeniøren 2012).

Pollutants in stormwater have been shown by researchers throughout the literature (Förster 1999; Eriksson 2002; Grant et al. 2003; Göbel et al. 2007; Hvitved-Jacobsen et al. 2010a; Björklund 2011). The content of pollutants changes with the catchment area, especially with the activities in the catchment. Stormwater from roads and parking areas contains metals, organic compounds such as e.g. polycyclic aromatic hydrocarbons (PAHs), phthalates (plasticizers) and oil components. Rooftops can release metals and green areas have been shown to contribute with pesticides (Revitt et al. 1990; Zgheib et al. 2011). Particulate matters are considered a polluting component in

stormwater. Total Suspended Solid (TSS) and turbidity are used to describe the concentration of particles found in water, and high TSS and turbidity indicate high numbers of particles in an aqueous sample. They do, however, not measure a certain size of the particles. TSS is analysed by filtrating a sample through a filter with a known mesh size, giving the weight per volume for the particles bigger than the chosen filter (EPA method 160.2). Turbidity is the density of particles in a sample by scattering at a selected wavelength. Techniques such as Dynamic Light Scattering (DLS) and Electrical Resistive Pulse (ERP) are used for measuring particle sizes, give a description of the particle size distribution (PSD) in an aqueous sample. The DLS and ERP techniques have been used to find PSD in stormwater, but not on a regular basis (Westerlund et al. 2006).

The interest in particles in stormwater relates to the evidence that particles are sorbing polluting compounds and, thereby, are able to transport the pollutants around in stormwater systems (Grant et al. 2003; Roesner et al. 2007; Kalmykova et al. 2013; Nielsen et al. 2015c – paper III). Stormwater particles $>0.45\text{ }\mu\text{m}$ will sediment in treatment facilities as detention ponds, thereby retaining and accumulating pollutants in the sediment. Large gravel particles with a surface of 2–64 mm will sediment quickly (seconds), while small silt particles (0.06–1 mm) will need hours to settle. Particulate matter such as colloids (having a large surface size, but a small volume) will take years to settle (Roesner et al. 2007; Dietrich 1982). Smaller particles, including colloids and nano-sized particles have been shown to be discharged from stormwater treatment facilities, thereby enhancing the transport of pollutants to receiving waters (Brown et al. 2003; Göbel et al. 2007; Kalmykova et al. 2013; Nielsen et al. 2015c – paper III; Nielsen et al. 2015e – paper V).

Phase separation of pollutant concentrations present in stormwater is described as: total, suspended, particulate and dissolved. The total fraction contains dissolved compounds, colloids, nano-sized particles, and bigger particles. The suspended fraction contains dissolved compounds, colloids, and nano-sized particles. The particulate fraction is defined as that which is retained on filters, often quantified by subtracting the suspended fraction from the total fraction or by measuring the concentration retained by the filter (Nielsen et al. 2015 – paper III).

The amount of particles found in stormwater depends on different conditions. TSS has been measured in a range of 0.5–5700 mg/L (Petersen et al. 2013), and turbidity of 1.5–400 NTU. Stormwater during the winter seasons will

often show high values of TSS and turbidity, due to de-icing agents used on roads and traffic areas. A long and pre-existing dry period will create an accumulation of particles on urban surfaces (Kim et al. 2007). The catchment from where the stormwater originates is also influencing the type and concentration of particles. Areas with high traffic intensities will release higher concentrations of particles, due to a higher level of wear and tear on roads and tyres, than less intensively trafficked areas (Grant et al. 2003).

The non-polar, hydrophobic PAHs are found to be associated with stormwater particles. The PAHs are considered carcinogenic, cause mutagenic effects in humans and biota, and are listed as some of the compounds most likely to cause effects on aquatic life or human health by the US EPA (Watts et al. 2010). Traffic activities have shown a positive correlation with increasing levels of PAHs in stormwater (Moilleron et al. 2002; Murakami et al. 2005; Van Metre et al. 2000). An important identified source of PAHs in stormwater are the aromatic-rich oils which were added to rubber tyres until 2010, when the EU banned the use of them (Directive 2005/69/EC; Norin & Strömvall 2004; Wik & Dave 2005).

The PAHs have shown, besides accumulating in urban road-side sediments and stormwater pond sediments, to accumulate in coastal estuarine and marine sediments. The concentrations in the sediments have increased over time, indicating multiple discharges associated with industrialisation and urbanisation, especially the release from vehicles and tear of asphalt (Bathi et al. 2012). Although some PAHs are naturally occurring from, for example, forest fires, volcanoes and wood burning, the majority of the PAHs found in stormwater are from anthropogenic sources, e.g. the release of petroleum products or combustion of organic matter, including coal. Regardless of the source, stormwater in urban areas is a major delivery system of PAHs to receiving water bodies (Stein et al. 2006).

1.1 Aim and Objectives of the PhD Thesis

In the present study, the overall aim is to document the presence and size distribution of colloids and nano-sized particles in stormwater and to quantify the particle-enhanced transportation of PAHs.

The focus in this thesis is, therefore, on natural and artificial colloids and nano-sized particles, as well as on PAHs in stormwater with the following specific objectives:

To characterise the particle size distribution of colloids and nano-sized particles in stormwater, and quantify the content of PAHs in the total, particulate, colloidal as well as dissolved fractions of stormwater.

To study the role of colloidal and nano-sized particles for the transport of PAHs in stormwater using stimulated stormwater and real stormwater.

To evaluate the performance of selected stormwater treatment technologies for colloidal and nano-sized particle pollution mitigation, in terms of removal efficiencies.

1.2 Methods and Overview of Thesis

Overall, the papers included in this thesis focus on the three different objectives described above, which are listed in **Table 1**. To fulfil the aims of this thesis, literature studies and fieldwork have been conducted and analysis methods already described in the literature have been used.

Table 1: The specific objectives of this thesis, showing the linked papers.

	Papers				
	I	II	III	IV	V
Characterisation of colloids and nano-sized particles in stormwater	x	x	x		x
To study the role of colloidal and nano-sized particles for the transport of PAHs in stormwater	x		x	x	x
Evaluate removal efficiencies of particulate matter, colloids and nano-sized particles, associated with metals and PAHs in stormwater treatment facilities		x	x		x

In the characterisation of the colloids and nano-sized particles, different methods for the PSD has been used. The methods have, prior to analysis of stormwater samples, been applied to simulated stormwater containing nano-sized humic acid colloids (HA-n) and nano-sized iron(III) particles (Fe-n). To describe the content of stormwater particles and their associated pollutants, stormwater has been collected from five different sites in Europe. The five sites, in combination with a short description of their catchment and stormwater treatment technique, are shown in **Table 2**.

Table 2: Description of sites, catchments, and treatment technology of the five different sites where stormwater samples were sampled for the experimental work.

City/Country	Site	Catchment	Treatment Technique
Lyon, France	Django Reinhardt	Industrial area of 1.85 km ² with 75% impervious surface ¹	Detention pond ¹
Gothenburg, Sweden	Gårda	Highway, roads, parking lots and employment office area. 0.051 km ² with 40% impervious surface ²	Seven combined underground sedimentation tanks ²
	Järnbrott	Roads, highway, 30% commercial and industrial area and 70% residential area. 4.78 km ² with 37% impervious surface ³	Stormwater pond ^{3, 4}
Bagsvaerd, Denmark	DemFil	3km ² residential area with small roads and low traffic ⁴	Disc filter filtration, with and without adding a flocculant ⁴
Albertslund, Denmark	Basin K	0.9km ² industrial area with 37% impervious surface ⁵	Detention pond ⁵

1: Sebastian et al. (2014), 2: Pettersson et al. (2005), 3: Strömvall et al. (2006), 4: Pettersson (1999), 5: Nielsen et al. (2015), 6: Vezzaro et al. (2015)

Chapter 2 of the thesis describes how urbanisation, stormwater and pollution, especially PAHs, are connected and explains the reasons why stormwater could be in conflict with the demands in the Water Framework Directive (Papers II, III and V).

Chapter 3 introduces colloids and nano-sized particles, and particulate matter in general in stormwater, and describes how colloids and nano-sized particles can contribute to enhanced transportation of PAHs. The different PSD methods are described and PSD results of simulated as well as sampled stormwater are shown (Papers I, II, III and IV).

In chapter 4, an overall description of different stormwater treatment techniques (with their benefits and drawbacks) is given using the results from papers II, III and V.

In chapter 5, results found in papers I–V will be discussed in relation to the overall aim and specific objectives of this thesis project.

2 Urbanisation and Stormwater

Urbanisation has a large influence on the quality of stormwater. Precipitation, e.g. rain, fog and snow, in urban areas will fall on roofs, roads, streets, gardens and green areas. Some of the precipitation will be removed by evapotranspiration and infiltration, and some will become surface runoff (stormwater) drained into the sewer system. Collection and treatment of stormwater can be controlled in different ways. One is by collecting the water in combined sewer systems for treatment at the wastewater treatment plant (WWTP), together with the wastewater. Another option is to collect the stormwater in a separate sewer system with discharge directly to receiving water or transport to a stormwater treatment facility. **Figure 1** illustrates some of the routes in which urban stormwater can be conveyed out of the urban area. As urban areas have increased in size and density over the last century, the areas covered with impervious surfaces have followed. The impermeable surfaces prevent the stormwater from infiltrating into the soil and, at the same time, creating runoff ways for the stormwater. In rural land, stormwater will infiltrate into the soil and the volume of stormwater reaching receiving waters will be much less than that of an urban area (Henze et al. 2004).



Figure 1: Stormwater routes in the urban area compared to the rural land. Impervious surfaces prevent the stormwater from leaching into the soil and a bigger volume of stormwater is entering stormwater treatment facilities compared to the rural land. (Illustrated by P. M. Nielsen, 2015).

The impervious surfaces and sewer systems create a high flow of urban stormwater, resulting in increased water flow from urban areas to WWTPs or receiving waters. The initial period of runoff stormwater will contain a higher concentration of suspended solid and other pollutants than later on in the runoff period; this phenomenon is known as the first flush (Gupta et al. 1996; Sansalone et al. 2004). **Figure 2** illustrates the increase in peak height, i.e. stormwater intensity and size, when the land is increasingly urbanised. The first flush will, besides causing a deterioration of the receiving water quality, also create a danger for erosion of river banks and a sudden flooding of receiving waters, together with a decreased treatment in the WWTP (Lee et al. 2002).

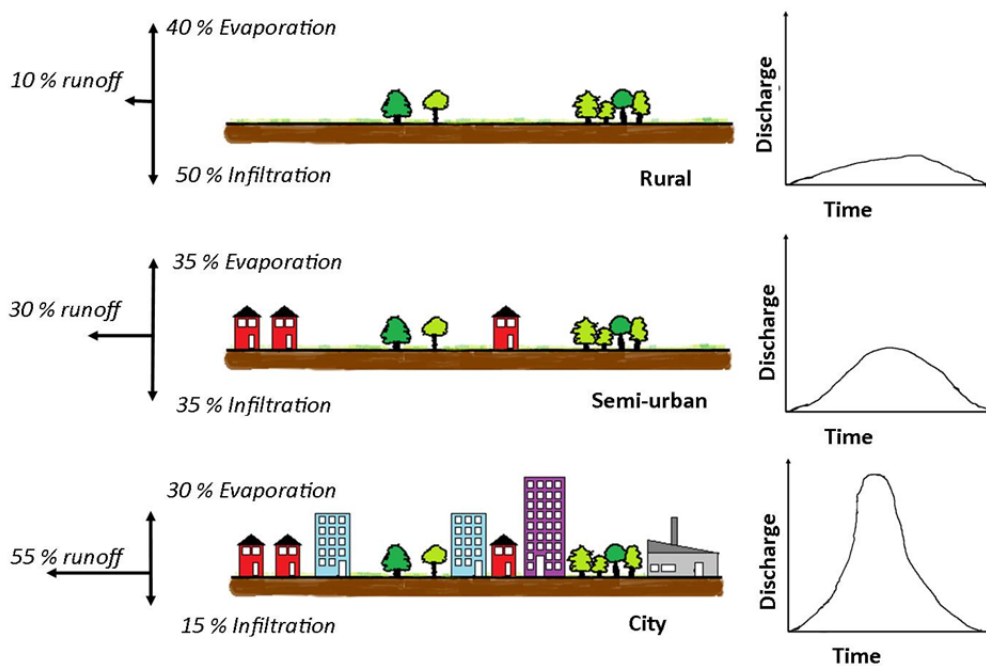


Figure 2: Illustration of how urbanisation creates a higher peak flow of stormwater during a rain event (modified from Arnold et al. 1996).

Even though a longer dry period is expected to create a higher concentration of pollutants in stormwater, there is no clear evidence of a correlation between the concentrations of pollutants found in the first flush and days of dry weather (Bertrand-Krajewski et al. 1998; Lee et al. 2002; Nielsen et al. 2015b – paper II). It has been shown that the rainfall intensity and duration were the most important parameters influencing the first flush load of TSS (Gupta & Saul 1996). The pollutants found in the first flush are often transported from the atmosphere (Gunawardena et al. 2013). Pollutants transported from the atmosphere to urban surfaces must be dissolved in the rain drops or sorbed to

particles in order to end up in stormwater (Seinfeld et al. 2006). Pollutants found in stormwater from roads are mainly from wet and dry atmospheric deposition and from the traffic (Göbel et al. 2007).

2.1 European Legislation of Stormwater

Implementation of the WFD in 2000 by the EU Parliament was to protect and restore clean water across Europe, and to ensure its long-term and sustainable use (WFD 2000/60/EC). The WFD has the aim as a minimum to achieve a “good status” in terms of biological and chemical, for all inland surface waters, transitional waters, coastal waters, groundwater and thereby, the receiving waters of stormwater by 2015. The “good” status describes the ecological and chemical status separately. The “good status” is generally defined as follows: *“The values of the biological quality elements for the surface water body type show low levels of distortion resulting from human activity, but deviate only slightly from those normally associated with the surface water body type under undisturbed conditions”* (WFD 2000/60/EC/annex V). This means that the authority has to define the biological quality of the surface water without human impact, and thereafter decide if the water is of good status.

The good chemical status is defined as *“.....the chemical status required to meet the environmental objectives for surface waters established in Article 4(1)(a), that is the chemical status achieved by a body of surface water in which concentrations of pollutants do not exceed the environmental quality standards established in Annex IX and under Article 16(7), and under other relevant Community legislation setting environmental quality standards at Community level”*. The directive does not state limitations for chemical compounds in discharged stormwater to surface water. Article 4 describes the objectives of management plans, and Article 16 the strategy plan *“...against pollution of water by individual pollutants or groups of pollutants presenting a significant risk to or via the aquatic environment, including such risks to waters used for the abstraction of drinking water”*. Annex IX contains the only specific discharge concentrations where compounds such as mercury (Hg), cadmium (Cd) and specific dangerous compounds such as the insecticide DDT (dichlorodiphenyltrichloroethane) and the organic solvent CCl₄ (tetrachloromethane) are described.

Environmental quality standards (EQS) for aquatic environments have been implemented in the Danish legislation for surface water, sediment and biota through a Statutory Order (BEK nr. 1022, 2010). The legislation distin-

guishes between a general long-term EQS, applied as an average concentration found in an aquatic environment over a year (may not be exceeded), or and a short-term (acute, 24 h) concentration allowed to exceed the long-term (general) standard. **Table 3** summarises selected organic and inorganic chemicals in general and short-term concentrations allowed in surface waters. The WFD only states the EQS for the receiving surface waters; nothing is stated about the quality of the water being discharged, or emission limit values.

Table 3: Danish Environmental Quality Standards (EQS) for selected inorganic and organic chemicals in surface waters (BEK 1022, 2010).

Compound	General ^a EQS for inland sur- face waters (µg/L)	Short-term ^b EQS for in- land surface waters (µg/L)
Organic		
<i>Naphthalene</i>	2.4	Not in use
<i>Acenaphthylene</i>	1.3	3.8
<i>Acenaphthene</i>	3.8	3.8
<i>Fluorene</i>	2.3	21.2
<i>Phenanthrene</i>	1.3	4.1
<i>Anthracene</i>	0.1	0.4
<i>Pyrene</i>	0.0046	0.023
<i>Fluoranthene</i>	0.1	1
<i>Chrysene</i>	0.014	0.014
<i>Benzo(a)anthracene</i>	0.012	0.018
<i>Benzo(a)pyrene</i>	0.05	0.1
<i>Benzo(b)fluoranthene</i>	0.03	Not in use
<i>Benzo(k)fluoranthene</i>	0.03	Not in use
<i>Benzo(ghi)perylene</i>	0.002	Not in use
Inorganic^c		
<i>Arsenic As</i>	4.3	43
<i>Barium Ba^d</i>	9.3	145
<i>Cadmium Cd</i>	0.08 – 0.25	0.45 – 1.5
<i>Cobalt Co^d</i>	0.28	18
<i>Chromium Cr (III and VI)</i>	3.4 – 4.9	17 – 124
<i>Copper Cu^d</i>	1	2
<i>Manganese Mn^d</i>	150	420
<i>Molybdenum Mo</i>	67	587
<i>Nickel Ni^d</i>	2.3	6.8
<i>Lead Pb^c</i>	0.34	2.8
<i>Strontium Sr</i>	210	553
<i>Vanadium V^d</i>	4.1	57.8
<i>Zinc Zn^d</i>	7.8	8.4

a) Average concentration over a year. b) Maximum allowed concentration for 24 hours. c) Dissolved concentration filtrated through a 0.45 µm filter or similar. d) Background concentration is taken into consideration.

2.2 Current Status of Water Framework Directive

The latest published status (2015) for the WFD is described by the European Environmental Agency (EEA). In 2009, 43% of the surface waters in Europe had achieved the status of good or a high ecological status. It is estimated that 53% of the surface water will have reached a good status in 2015, which, however, is lower than that set by the directive. It is observed that rivers and transitional waters are in worse condition than lakes and coastal waters. Ecological status concerns are mostly seen for surface waters in Central and Northwestern Europe, where the population is dense and agriculture is intensive (EEA 2015).

For the chemical status, around 10% of lakes and rivers have a poor chemical status, and PAHs and toxic metals are highly contributing to this. Twenty-five per cent of the groundwater around Europe is dealing with poor status, where nitrate is the primary cause. Forty per cent of the rivers and lakes around Europe are still lacking assessment of their chemical status (EEA 2015).

Discharge of pollutants into stormwater may contribute to the low chemical status identified for the surface waters. Even though emission control strategies, such as the exchange of fuels and change of tyre additives, have been implemented in the EU, increased concentration levels of PAHs have been found in urban sediments in stormwater treatment facilities (Andersson et al. 2014).

2.3 Stormwater Pollutants

Stormwater from urban areas contains pollutants which can affect the quality of receiving surface waters and groundwater. Metals such as Pb, Zn, Cu, and Cd are, together with organic compounds such as PAHs and particulate matter (TSS) all found in stormwater (Grant et al. 2003). Besides these parameters are Electrical Conductivity (EC), nutrients (total phosphorus and total nitrogen), Non-Volatile Organic Carbon (NVOC), TOC (Total Organic Carbon) and Biological Oxygen Demand (BOD), which are all parameters used in the literature to describe the environmental composition and condition of stormwater (Göbel et al. 2007). In **Table 4** literature values for pH, TSS, NVOC and EC are summarised.

Table 4: Physical and chemical parameters in road and roof runoff samples.

Physical and Chemical Parameters					
Reference	Runoff source	pH	TSS (mg/L)	NVOC (mg/L)	EC (μ S/cm)
Makepeace et al. 1995	Roof and road	4.5 – 8.7	1 – 36,200	–	–
Eriksson 2002	Road	5.5 – 9.3	4.0 – 4800	4.5 – 14	8.8 – 110,000
	Roof	3.8 – 11	–	–	10 – 1586
Göbel et al. 2007	High traffic density	6.4 – 7.9	66 – 937	–	108 – 2436
	Roof	4.7 – 6.8	13 – 120	–	25 – 269
Nielsen et al. 2015b – paper II	Roof and road	6.8 – 8.2	19 – 98	9.0 – 364	146 – 963
Nielsen et al. 2015c – paper III	Roof and road	6.5 – 7.0	10 – 659	3.8 – 24	50 – 836
Nielsen et al. 2015e – paper V	Roof and road	4.6 – 7.6	24 – 178	247 – 302	366 – 27,000

– = no data, TSS = Total Suspended Solid, EC = Electrical Conductivity, NVOC = Non-Volatile Organic Compound.

Table 4 shows a large variation for all of the parameters. The data shown for Makepeace et al. (1995), Eriksson (2002) and Göbel et al. (2007) are all reviewed data from different sites, while the data from Nielsen et al. (2015b – paper II), Nielsen et al. (2015c – paper III) and Nielsen et al. (2015e – paper V) are experimental data from three different sites. The pH values listed in **Table 4** show that pH in stormwater can be acidic, neutral and basic, and no pattern was observed for the runoff surface. The measurements within the same site also showed an event-to-event variation, but also a catchment-to-catchment variation.

The TSS concentrations range from 1 to 36,200 mg/L, with the highest concentrations found for stormwater from trafficked areas. Despite that TSS found by Nielsen et al. (2015 – paper III) came from a residential area with low traffic activity, a TSS concentration of 659 mg/L was found in one event. This was explained by the use of de-icing agents on the roads, contributing to the total mass of particulate matter and causing particles to flocculate or coagulate. In the three papers by Nielsen et al. the filter mesh size used to measure the TSS concentration was 0.7 μ m. In the reviews by Makepeace et al. (1995), Eriksson (2002) and Göbel et al. (2007), the filter mesh size is not mentioned. A filter with a mesh size of 0.45 μ m will give a higher concentration of TSS than a filter with a mesh size of 0.7 μ m. Even though it is im-

portant information to give for the TSS measurements, the findings in **Table 4** shows a catchment-to-catchment variation and also an event-to-event variation, which cannot be explained by the different filter mesh sizes.

The TOC is more frequently quantified in stormwaters than the NVOC, but since the NVOC are not removed in the stormwater by volatilisation, as some of TOC can be anticipated to do, the NVOC will be transported together with the stormwater. The concern for the NVOC in the environment is that it has been shown to cause mutagenic effects, allergies and a risk of cancer in aquatic species (Mahbub et al. 2011, 2012). As seen for the TSS concentrations, the NVOC are found in the highest concentrations in stormwater from catchments with traffic activities (Nielsen et al. 2015b – paper **II**; Nielsen et al. 2015e – paper **V**). This is also expected since motor oil and lubricants both contribute to NVOC in stormwater (Mahbub et al. 2011).

The EC is used to describe the salt concentration in stormwater, where a high EC indicates a relatively high salinity. As seen for the TSS and NVOC, EC values are higher for stormwater which has been in contact with road surfaces than for stormwater in contact with roofs. A high EC can, besides affecting the living conditions for the aquatic community, also cause particles in stormwater to flocculate and aggregate (Nielsen et al. 2015c – paper **III**).

2.4 Inorganic Pollutants in Stormwater

Förster et al. (1996, 1999) have shown that the concentration and chemical content of pollutants in stormwater depend on the runoff surface. These surfaces can be divided into three groups (Göbel et al. 2007):

- Partly sealed surfaces (overgrown soil in backyards, urban green spaces and porous paving).
- Impermeable roof surfaces
- Impermeable road surfaces

The results in **Table 4** indicate that stormwater from road surfaces have the highest concentrations of TSS, NVOC and EC, even though 50 % of the urban stormwater in industrialised countries is in contact with roof surfaces (Förster 1996). Roof surfaces, on the other hand are shown to release chemical compounds to the stormwater. A variety of materials are used for roof surfaces, with some containing inorganic compounds such as metals. Wear and decay will release metals to the roof runoff. Simmons et al. (2001) inves-

tigated 125 households in Auckland, New Zealand, which collected stormwater from roofs and used it as drinking water. Metals were present in elevated concentrations and were attributed to the roofing materials. Van Metre et al. (2003) has shown that stormwater from buildings in Austin, Texas, USA, contributed with 55% of the total amount of metals in stormwater.

Literature values of metal concentrations found in stormwater from roofs and roads are shown in **Table 5**. Here the 13 metals from the Danish Directive 1022 (Bek 1022, 2010) are listed with recorded concentration ranges. In these findings, only Grant et al. (2003), Nielsen et al. (2015b – paper **II**) and Nielsen et al. (2015c – paper **III**) distinguish between metals in the different fractions: total, suspended and particulate. Makepeace et al. (1995), Eriksson (2002) and Göbel et al. (2007) describe findings in the literature where no fraction was considered. Compounds such as Cr, Cu and Zn are found in higher concentrations from roof runoff compared to the road runoff according to Eriksson (2002), while Göbel et al. (2007) only found a higher concentration in roof runoff compared to road runoff for Zn. The suspended metal concentrations found by Grant et al. (2003) are higher than the ones found by Nielsen et al. (2015b – paper **II**) and Nielsen et al. (2015c – paper **III**). The catchment for the findings given by Grant et al. (2003) is not described and dose hampering explanations for the observed differences. The total suspension concentrations measured by Nielsen et al. (2015b – paper **II**) and Nielsen et al. (2015c – paper **III**) are comparable to the findings by Makepeace et al. (1995), Eriksson (2002) and Göbel et al. (2007). The catchments from which the stormwater in Nielsen et al. (2015b – paper **II**) and Nielsen et al. (2015c – paper **III**) originated concern an industrial area (2015b) and a residential area (2015c). The concentrations of Cu, Mn, Ni and Pb were highest in the residential areas. Because of the lower traffic density compared to the industrial area, the higher concentration cannot be explained by traffic, but could be from the roofs.

Table 5: Comparison of selected metals found in stormwater (µg/L). All of the metals listed are found on the EQS list.

Reference	Surface	As	Ba	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	V	Zn
Makepeace et al. 1995	Roof and road	0.1-210	66-87	0.05-13730	1.3-5.4	1-2300	0.06-1410	7-3800	-	1-49000	0.5-26000	7.2-8.5	0.7-22000
Eriksson 2002	Road	0.1-340	40-86	<0.05-2000	0.08-6.7	<0.05-210	<0.5-1250	0.5-1647	1.0-20	<0.02-436	<0.5-6400	7.2-29	1.73-25500
	Roof	<5-19	-	0.04-32	-	1.4-510	1.1-4500	-	-	2.6-70	1.1-2764	-	<0.5-49942
Grant et al. 2003 (sus con) ^a		-	-	2-200	-	6-30	13-100	-	-	5-70	5-24	-	210-3800
Grant et al. 2003 (Par con) ^b		-	-	2-4	-	30-80	30-100	-	-	20-7400	50-90	-	170-640
Göbel et al. 2007	Road	-	-	0.3-13	-	6-50	97-104	-	-	4-70	11-525	-	120-2000
	Roof	-	-	0.2-1.0	-	2-6	6-3.4	-	-	2-7	2-493	-	24-4880
Nielsen et al. 2015b – paper II (Total con) ^c	Roof and road	-	-	-	-	-	7.3-15	43-82	-	2.3-9.8	2.7-8.7	-	26-47
Nielsen et al. 2015b – paper II (sus con) ^d	Roof and road	-	-	-	-	-	5.1-12	-	-	2.2-7.9	3.1-3.4	-	13-29
Nielsen et al. 2015c – paper III (Total con) ^c	Roof and road	2.1-9.5	-	-	1.6-6.7	2.3-20	8-95	19-778	-	4.7-19	2.1-37	-	-
Nielsen et al. 2015c – paper III (sus con) ^d	Roof and road	2.9-14	-	-	<0.5-1.5	2.3-3.4	2.6-14	2.4-258	-	1.6-18	1.4-3.1	-	13-45

- = no data, a= suspended concentration after a 0.45 µm filter, b = particulate concentration on a 0.45 µm filter, c = total concentration d = suspended concentration after a 0.7 µm filter.

In Nielsen et al. (2015b – paper II) stormwater from five sites in Europe was compared according to its TSS, turbidity, pH, NVOC, EC, metals and PAH concentrations. A correlation between the TSS concentration ($>0.45\ \mu\text{m}$) and the total metal concentration was found, suggesting that metals are associated with the TSS (**Figure 3**). There was no correlation between the dry weather period and the metal concentrations measured were found on this study; these results are confirmed by findings in by Bertrand-Krajewski et al. (1998) and Lee et al. (2002).

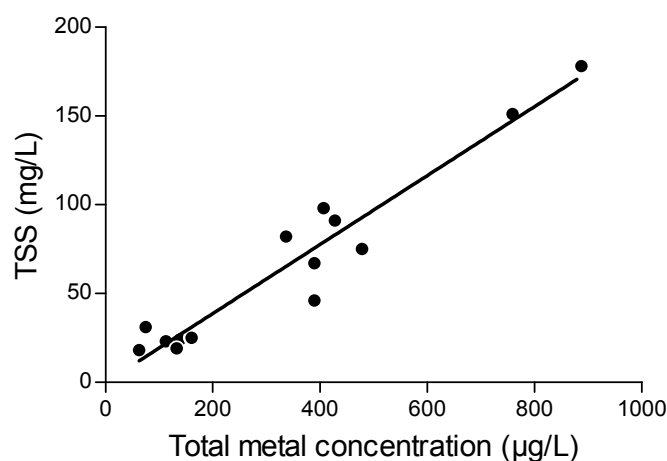


Figure 3: Correlation between Total Suspended Solids (TSS) concentrations and measured total metal concentrations from 17 inlet samples from five sites in Europe. $y=0.194x-0.109$, $R^2 = 0.93$. (data from Nielsen et al. 2015b – paper II).

2.5 Polycyclic Aromatic Hydrocarbons in Stormwater

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds released from both natural and anthropogenic sources. Wood burning and wildfires contribute to the PAHs in an aquatic environment together with the release of petroleum products and combustion of organic compounds. Regardless of the type of source, stormwater in urban areas discharges PAHs to surface waters (Stein et al. 2006).




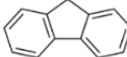

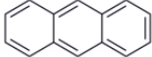
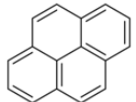
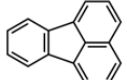
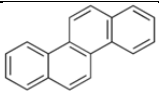
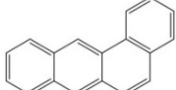
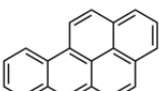
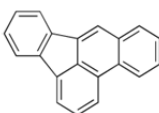
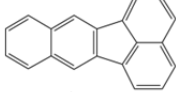

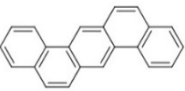
2.5.1 Polycyclic Aromatic Hydrocarbons as Compounds

PAHs generally occur as mixtures of different PAHs and not as single compounds. More than 100 different PAHs are created during incomplete burning of coal, oil, gas, wood, garbage or other biomass, such as tobacco and charbroiled meat. Seventeen of the PAHs are described more often in the literature due to: being more harmful, the frequency of being exposed to these 17

PAHs being higher than for other PAHs and these being the PAHs found in the highest concentration in the environment (ATSDR, 1995). **Table 6** gives the molecular structures, molecular weight, Log K_{ow} (octanol-water partitioning), Henry's law's constant (K_H) and water solubility of the PAHs investigated during experiments in Nielsen et al. 2015b – e (paper **III – IV**). The K_{ow} is the partition coefficient for an organic compound between water and octanol (lipid) and describes the potential of a neutral, lipophilic substance to bio-accumulate in aquatic organisms. The K_H describes the partitioning of a compound between the water and air phase at equilibrium and is used as indicator for the compound's potential to volatilise (ATSDR, 1995). The 15 PAHs in Nielsen et al. 2015b-e (paper **III-IV**) were chosen due to their chemical and physicochemical differences and their structural variation with different numbers of rings. The different number of rings makes it possible to group the PAHs into three groups, following their molecular weight:

- Low-molecular weight (LMW PAHs): naphthalene, acenaphthene and acenaphthylene (two- and three- ring structures).
- Medium-molecular weight (MMW PAHs): fluorene, phenanthrene, anthracene, fluoranthene and pyrene (three- and four- ring structures).
- High molecular weight (HMW PAHs): benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene (four- to six- ring structures).

Table 6: Physicochemical and chemical parameters for 15 selected PAHs. The PAHs are listed by molecular weight (ATSDR 1995).

Group	Compound	Molecular structure	Molecular weight (g/mol)	Log K_{ow}	K_H (atm*m ³ /mol)	Water solubility (mg/L)
LMW ^a	Naphthalene (Nap)		128.17	3.37	4.83×10^{-4}	31.69
	Acenaphthylene (Acy)		152.19	4.07	1.45×10^{-3}	3.93
	Acenaphthene (Ace)		154.21	3.98	7.91×10^{-5}	1.93
MMW ^a	Fluorene (Flu)		166.22	4.18	1.0×10^{-4}	1.68
	Phenanthrene (Phe)		178.23	4.45	2.56×10^{-5}	1.20
	Anthracene (Ant)		178.23	4.45	1.77×10^{-5}	0.076
	Pyrene (Pyr)		202.25	4.88	1.14×10^{-5}	0.077
	Fluoranthene (Flt)		202.26	4.90	6.5×10^{-6}	0.20
HMW ^a	Chrysene (Chr)		228.28	5.16	1.05×10^{-6}	2.8×10^{-3}
	Benzo[a] Anthracene (BaA)		228.31	5.61	1.10×10^{-6}	0.01
	Benzo[a]pyrene (BaP)		252.31	6.06	4.9×10^{-7}	2.3×10^{-3}
	Benzo[b] Fluoranthene (BbF)		252.31	6.04	1.22×10^{-5}	1.2×10^{-3}
	Benzo[k] Fluoranthene (BkF)		252.31	6.06	3.87×10^{-5}	7.6×10^{-4}
	Benzo[ghi] Perylene (BghiP)		276.33	6.5	1.44×10^{-7}	2.6×10^{-4}
	Dibenz[ah] Anthracene (DBahA)		278.35	6.84	7.3×10^{-8}	5×10^{-4}

a: LMW = low-molecular weight, MMW = medium-molecular weight, HMW = high-molecular weight

2.5.2 Sources and Occurrences of PAHs in Stormwater

The water solubility for the PAHs decreases with the increasing number of aromatic rings, naphthalene (two rings) is therefore more soluble than dibenz[ah]anthracene (five rings). Atmospheric PAH will reach urban surfaces by rainfall or by dry deposition. Other sources of PAHs pollution are: tyre particles, leaking of vehicle oils, vehicle exhaust, crumbling asphalt and parking lot sealants (ATSDR 1995, Maliszewska-Kordybach 1999; Brown et al. 2003; Eriksson et al. 2007). The PAHs will be subjected to long- and short- time atmospheric transportation before being removed by wet or dry deposition. In the atmosphere LMW PAHs and light MMW PAHs will be found in the vapour phase, while heavy MMW PAHs and light HMW PAHs will be found in both the vapour phase and particulate phase. The HMW PAHs are found predominantly in the particulate phase (ATSDR 1995). Deposition of PAHs from the atmospheric phase onto urban surfaces and stormwater varies with the individual PAH. PAHs sorbed to particles are most likely to be found in dry deposition while PAHs in the vapour phase will be found in wet deposition.

Concentrations of PAHs in stormwater can vary between catchments and from one event to another. Hwang and Forster (2006) have investigated PAHs in stormwater from an urban area with small-scale industry. The stormwater is discharged into the Anacostia River in the state of California, USA. The results are compared with previous studies from the same area and stormwater from similar catchments. Sebastian (2013) has measured PAHs in stormwater entering a detention pond in Lyon (France). The pond receives stormwater from an industrial area. In **Table 7**, their results are shown together with results from a similar Danish catchment (Albertslund) (Nielsen et al. 2015b – paper II) and a Danish residential catchment (Bagsværd) (Nielsen et al. 2015c – paper III) and a Swedish traffic area and a Swedish residential/traffic/commercial area (Nielsen et al. 2015e – paper V). The comparison shows a variation in concentration among the PAHs between the eight catchments, but no big variation in the relative composition of the PAHs among the sites.

Table 7: PAH concentrations (µg/L) found in total fractions of stormwater at seven different sites.

Site	Nap	Acy	Ace	Flu	Phe	Ant	Pyr	Flt	Chr	BaA	BaP	BbF	BkF	BghiP	DBaH	Reference
Albertslund, DK¹	<0.01-0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	Nielsen et al. (2015b) – paper II
Bagsværd, DK¹	0.1 - 0.34	0.02 - 0.05	BDL	0.02 - 0.09	0.02 - 0.09	0.07 - 0.38	0.42 - 1.94	0.2 - 0.98	0.0 - 0.3	0.07 - 0.28	0.04 - 0.28	0.04 - 0.25	0.03 - 0.4	0.02 - 0.29	0.05 - 0.31	Nielsen et al. (2015c) – paper III
Gårda, SW¹	<0.03 - 5.68	<0.02 - 3.23	<0.01	<0.01 - 0.50	0.19 - 1.03	0.13 - 1.24	1.14 - 8.37	0.87 - 7.39	2.38 - 4.39	3.24 - 5.57	9.02 - 18	1.89 - 1.99	2.37 - 4.62	2.39 - 2.72	<0.17 - 1.17	Nielsen et al. (2015e) – paper V
Järnbrott, SW¹	<0.03 - 9.4	<0.02 - 0.14	<0.01 - 2.6	0.01 - 4.7	0.15 - 1.8	0.18 - 4.4	4.71 - 7.6	4.69 - 6.3	2.30 - 7.41	2.62 - 8.8	7.52 - 27	1.56 - 3.0	2.32 - 5.9	2.04 - 3.5	<0.17 - 0.87	Nielsen et al. (2015e) – paper V
Lyon, F¹	0.01 - 1.1	0.03 - 0.08	0.01 - 0.2	0.01 - .04	0.02 - 0.14	0.005 - 0.03	0.008 - 0.25	0.006 - 0.22	0.002 - 0.11	0.03 - 0.07	0.007 - 0.09	0.002 - .18	0.2 - 0.6	0.02 - 0.11	-	Sebastian (2013)
Columbia, USA¹	-	-	-	0.06	0.48	0.06	0.47	0.64	0.62	0.28	0.42	0.98	-	0.46	0.39	Hwang and Forster (2006)
Anacostia River, USA¹	0.02 - 0.06	0.002 - 0.03	0.003 - 0.03	0.009 - 0.15	0.03 - 0.34	0.005 - 0.12	0.07 - 0.77	0.09 - 1.38	0.05 - 0.52	0.02 - 0.34	0.03 - 0.45	0.06 - 0.73	0.03 - 0.40	0.02 - 0.55	0.04 - 0.51	Hwang and Forster (2006)
Milwaukee, USA¹	-	<8.2	<3.4	<0.60	<0.17 - 0.40	<0.12 - 0.37	0.58 - 6.0	0.80 - 8.5	0.34 - 4.0	0.18 - 2.0	0.300 - 4.0	0.38 - 4.40	0.22 - 2.1	0.32 - 2.7	0.38 - 4.4	Hwang and Forster (2006)

- = no data , 1: DK = Denmark, SW = Sweden, F = France, USA = United States of America.

The PAHs occurring in the highest concentration in the stormwater samples are Nap, Pyr, Flt, BaPyr, BbF and BghiP. In Albertslund, Denmark, only four of the PAHs were quantified and the stormwater from Lyon, France showed nearly all of the PAHs, but at lower concentrations compared to the stormwater from USA. Here both studies showed that all of the selected PAHs were present in stormwater. The stormwater collected in Lyon (France) were showing similar concentrations as for the catchment in Albertslund and Bagsværd (Denmark). The catchments of Lyon and Albertslund are similar, both with industrial activity. An intra-catchment variation was found for the concentration of the PAHs. The Bagsværd site shows higher concentrations of PAHs than the light industrial Albertslund site. Compared to the sites in Anacostia, Columbia and Milwaukee, also containing industrial catchments, the findings in the two sites in Denmark were in the same concentration range, but lower. The findings in Nielsen et al. (2015e – paper V) showed higher PAHs concentrations in stormwater from the two sites in Sweden and is explained by the higher traffic load. The findings in Hwang and Forster (2006) show that the traffic load is correlated with the PAHs levels (**Table 7**).

3 Particulate Matter, Colloids and Nano-sized Particles in Stormwater

Particulate matter in stormwater is found in the size range of nm to cm (Grant et al, 2003; Roemer et al, 2007). Particulate matter in stormwater has traditionally been described as total, particulate and dissolved. The “particulate” fraction usually consists of the particles caught on a 0.45 μm filter (the TSS), while the “dissolved” fraction describes the content in the filtrate passing the filter. These three fractions are insufficient to fully describe and understand the behaviour and effects of particulate matter in stormwater, especially because the fractions do not consider the colloidal and nano-sized particle fractions (Lead et al. 1997). Today it is known that the dissolved fraction is not a truly dissolved fraction but contains colloids and are therefore often determined the “suspended fraction” (Brown et al. 2003; Kalmykova et al. 2013; Nielsen et al. 2015b – paper **II**; Nielsen et al. 2015c – paper **III**; Nielsen et al. 2015e – paper **V**).

Colloids and nano-sized particles have negligible settling velocities, as their small mass has a low gravitational force compared to surface frictional forces. The boundaries between colloids and nano-sized particles are overlapping (**Figure 4**), since nano-sized particles are defined as solid particles with one or more dimensions in the order of 1 – 100 nm (SCE-NIHR/002/05), while the colloidal material is defined as having at least one dimension between 1 nm and 1 μm (Gilbert et al. 2009). The small size of the colloids and nano-sized particles creates a long settling time (years), making them able to travel over long distances. Larger particles, such as those in particulate matter will settle in minutes or hours and therefore, are not transported so far (Degrémont 1991).

Particulate matter creates concern, especially in an aquatic environment, where the particles play a role as vectors for many chemicals by providing a surface area for the partitioning of chemical compounds (Sansalone and Kim 2008), and may have detrimental effects on the aquatic ecosystem, e.g. fish (Bash et al. 2001). Particles, colloids and nano-sized particles are all able to sorb pollutants and have been shown to be associated with metals and PAHs in stormwater (Brown et al. 2003; Göbel et al. 2007; Kalmykova et al. 2013; Nielsen et al. 2015b – paper **II**; Nielsen et al. 2015c – paper **III**; Nielsen et al. 2015e – paper **V**). The low settling velocity for the colloids and nano-sized particles has shown to create a concern for enhanced transport of pollutants

into receiving waters of stormwater (Buffle et al. 1995; Gustafsson et al. 1997; Lead et al. 2006; Nielsen et al. 2015e – paper V; Rees et al. 1990).

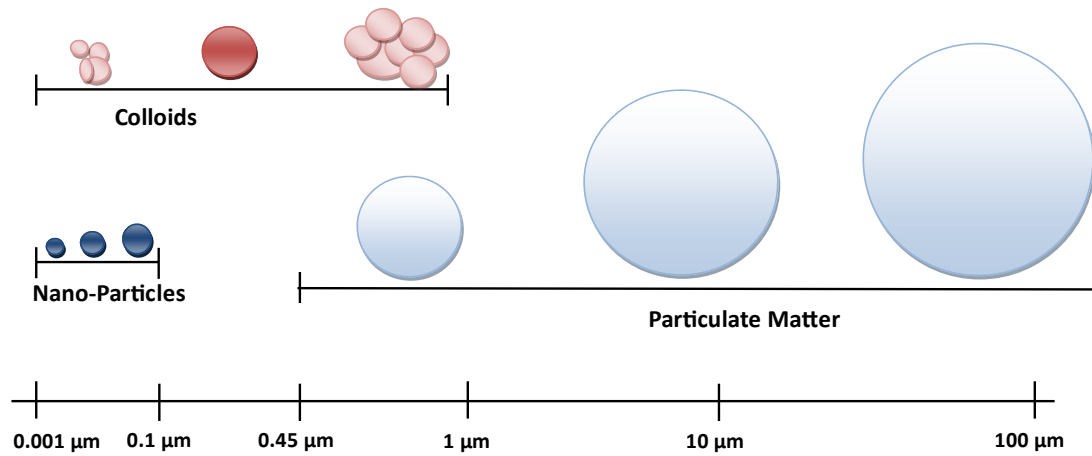


Figure 4: Illustration of size overlaps of particulate matter, colloids and nano-sized particles found in stormwater.

Particles in stormwater originate from different sources, such as windblown soils from nearby land use, tyre and brake wear, vehicle exhaust, road paint, and pavement degradation (Kayhanian et al. 2012). Tyre wear is contributing to high amounts of particles in stormwater. It is estimated that $(7.3 - 500) \times 10^3$ tonnes of particulate matter are released from tyres on a yearly basis in countries such as Denmark, Germany, Great Britain, Sweden and the USA. Most of the particles are large enough to deposit on the road, furthermore, close to the road, only 5 % or less will become airborne particles. Therefore most of the particles will be removed during runoff events or street cleaning (Wik & Dave 2009).

3.1 Characterisation of Particulate Matter, Colloids and Nano-sized Particles in Stormwater

Particulate matter in stormwater has for many years been described as the TSS. Turbidity is another method to determine the concentration of particulate matter in stormwater. It has been showed that there is a correlation between the TSS and turbidity (Métadier & Bertrand-Krajewski 2012). Therefore is one of the other used to determine either TSS or turbidity. In Nielsen et al (2015b - paper II) were stormwater from seven sites compared. For all of the sites were both TSS and the turbidity measured and as seen in **Figure 5** was there a correlation between the two stormwater parameters.

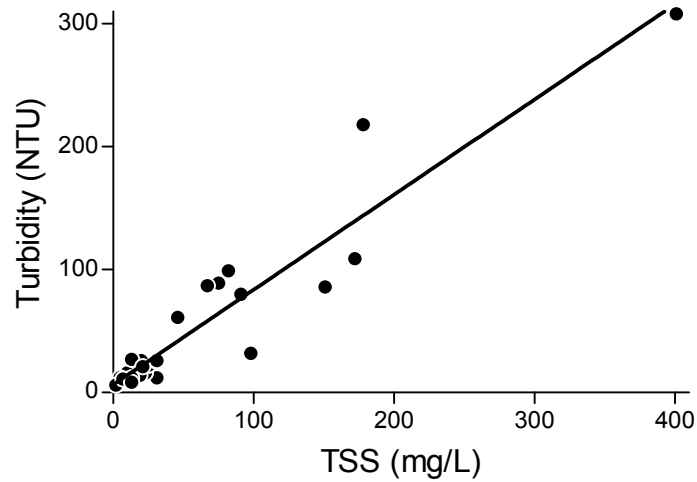


Figure 5: Correlation between measured turbidity and measured TSS values. $=0.77x+6.25$, $R^2 = 0.89$. (Data from Nielsen et al. 2015b – paper II).

Turbidity is measured by detecting how much light are scattered by the suspended particles in the stormwater. Turbidity has that advantage compared to TSS that it is possible to measure in the field and do not need laboratory equipment. Therefore can turbidity be measured onsite, where samples for TSS have to be transported back to the laboratory. The two techniques do not describe the particulate particle size and therefore are they not giving the PSD of the particles in stormwater.

Determination of PSD in the μm range has been performed for a longer time period than for nano-sized particles and colloids in the nm range. The settling velocity of the particles in sediment and stormwater samples has been used to find the PSD of stormwater particulate matter (Bäckström 2002; Kim & Sansalone 2008; Zander 2005). The Electrical Resistive Pulse (ERP) technique used by Coulter counters has also been used to find the PSD for particulate matter in stormwater, stormwater sediment and snowmelt (Borst et al. 2003; Westerlund et al. 2006). The particles were in the range of 1 – 24,500 μm in re-suspended sediment or particles collected from roads and streets, together with particles in stormwater. PSD of re-suspended sediment is limited to settleable particles and fine suspended particles will not be detected with this approach. Electrical Resistive Pulse and settling techniques have application limitations for colloids and nano-sized particles in aqueous samples. The sizes of the particles are too small to be registered by the ERP and their settling, if any are found, are too slow to be measured.

Dynamic Light Scattering techniques use the natural movement of particles in suspension (Brownian motion), and by measuring the distance that the particle travels over time, the spherical hydrodynamic diameter of a particle can be calculated (Goldburg 1999). By applying a laser to a liquid sample, the laser will hit the surface of a particle and the light will be scattered. Thus, DLS is a technique able to characterise the PSD of colloids and nano-sized particles in stormwater. The inherent light clouded structure of colloids could hamper the analysis, as it causes low scattering. A disadvantage when using the DLS technique for measuring particles in stormwater is that particle settling can be mistaken for Brownian motions or the settling motion can overshadow the Brownian motions, yielding false positives or no quantifiable results. Smaller nano-sized particles or colloids can be shaded by bigger particles, thereby being impossible to detect. To prevent settling or shadowing, measurements on PSD of colloids and nano-sized particles should always be conducted on the suspended fraction of stormwater. A good resolution can be obtained if information such as the refractive index of the liquid and poly-dispersed index of the particles is given. Particle measuring techniques using DLS can have problems, especially with coloured samples (Hassellöv et al. 2008; Malvern 2004; Brar et al. 2011).

Other relevant techniques for PSD determinations are: Field Flow Fractionation (FFF) and Transmission Electron Microscopy (TEM). The FFF technique separates particulate matter, colloids and nano-sized particles in a flow cell. A wide range of detectors are used to determine the PSD after separation, and often are DLS coupled to the FFF cell. Using the technique on stormwater could create a better separation of the colloids and nano-sized particles before detection, but the FFF needs a carrier liquid in the cell, and ionic strength and pH changes can occur when mixing the stormwater with the carrier liquid (Gimbert et al. 2003; Giddings 1993). Microscopy techniques such as TEM make it possible to visualise the particles in stormwater and, at the same time measure their sizes. Sample preparation is required and the liquid matrix of the stormwater has to dry on a grit before measurement. This could create flocculation or aggregation of the particles (Tiede et al. 2008).

3.1.1 Zeta Potential and Stability in Stormwater

The ability of colloids and nano-sized particles to flocculate or agglomerate in stormwater is, among other things determined by their surface charge and the outer surface potential. The zeta potential is defined as the potential difference across phase boundaries between a solid and a liquid. Determination of the zeta potential will also give the surface potential of a particle or colloid

(Malvern, Zeta Potential). The zeta potential is related to the electrophoretic mobility of a particle in a liquid and is given as mV. The electrophoretic mobility is used together with the thickness of the electrical double layer, to calculate the zeta potential (Malvern, Zeta Potential).

Particles with zeta potentials between -10 and $+10$ mV are considered approximately neutral, unstable and, thus likely to flocculate, while particles with zeta potentials greater than $+30$ mV or less than -30 mV are considered strongly charged and, therefore, are repelling other particles (Clogston et al. 2011). Changes in the pH in the liquid surrounding the particles will also change the zeta potential of the particles. The point where the particle charge is neutral is called the zero point charge, and can be used for stormwater, to determine at which pH particles are most likely to flocculate/aggregate, thereby increasing in size and starting settling.

Zeta potentials of particles in stormwater from a highway and detention pond sediment were analysed by Kayhanian et al. (2012). The zeta potentials for the highway stormwater gave values from -20 to -23 mV, indicating a relatively low tendency to aggregate. The samples collected from the sediment in the detention pond all showed negative values and ranged from approximately -13 mV to -50 mV. In Nielsen et al. (2015b – paper II), zeta potentials in stormwater from five different catchments (residential areas, different highways and industrial areas) were found to be from -15.6 to -29.6 mV, indicating a negative surface charge on the particles, consistent with particles having a composition of organic acids e.g. fulvic and humic acid (Nielsen et al. 2015c – paper III) and/or hydrolysed clay surfaces. The zeta potential of stormwater particles from a highway bridge was also found to be around -20 mV (-22.6 ± 1.2 mV) by Sansalone & Kim (2008).

3.1.2 Characterising of Particulate Matter Using Coulter Counter

The Coulter counter principle using the ERP technique is developed to count blood cells, minerals, bacteria, etc. in aqueous samples with a diameter in the μm size range. The technique works by measuring a change in the electrical field in a liquid. When a particle passes through two electrodes submerged in a liquid sample, a change in the electrical current will occur and this change is used to calculate the size of the particle (Azom 2015).

Westerlund et al. (2006) used the Coulter counter to determine the PSD of particles in snowmelt runoff and stormwater over a 3-months period in a catchment with approximately 7400 vehicles/day in Sweden. Westerlund et al. (2006) found that 87–98 % of the particles were found in the size range 4–

9 μm and less than 2 % were found in the range of 25-120 μm . Coulter counter findings in a similar catchment, but with a higher concentration of industry, in Lyon (France) and Albertslund (Denmark) also showed PSD with up to 100 % of the particles smaller than 10 μm in diameter (Nielsen et al. 2015b – paper II). In the same study, the PSD of particles in stormwater samples from a residential area (Bagsværd, Denmark) and a catchment containing a highway was also included (Gårda and Järnbrott, Sweden). As found by Westerlund et al. (2006), the PSD of the particles from the catchments (**Figure 6**) showed that 95 % of the particles in the stormwater were smaller than 10 μm in diameter.

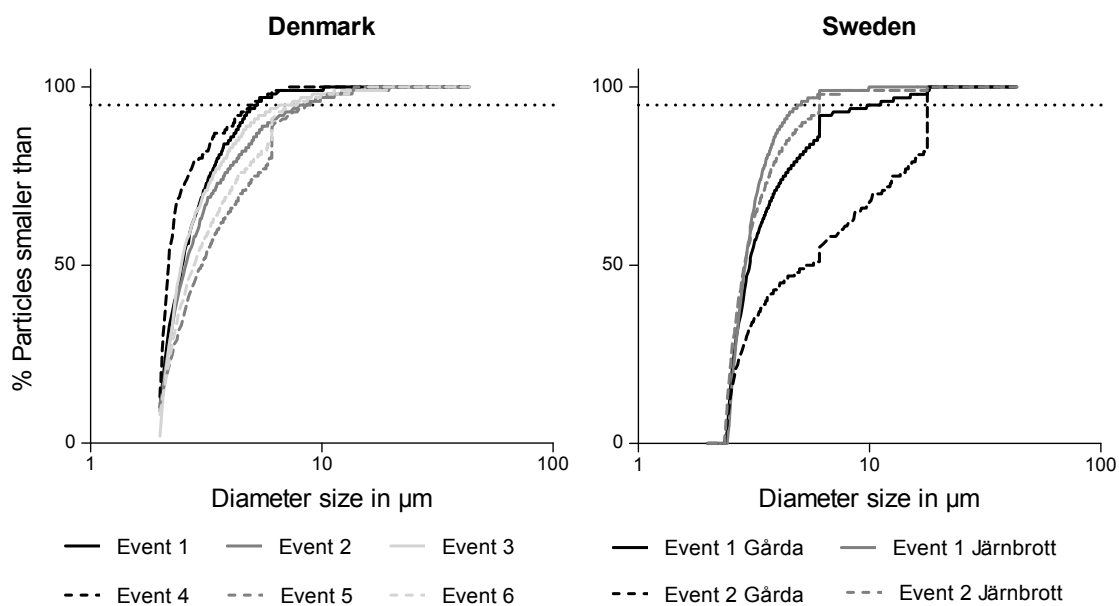


Figure 6: Particulate matter in collected stormwater samples measured using the Coulter counter principle at three different sites (note the logarithmic x-axis). (Nielsen et al. 2015c – paper III; Nielsen et al. 2015e – paper V)

By using a settling method did Li et al. (2006) find particles in stormwater from three different highway sites in the same size range as Nielsen et al. (2015b – paper II). With the settling method Li et al. (2006) found that 90% of the particles were less than 10 μm . Other methods applied have shown broader PSD of particulate matter in stormwater. Kim & Sansalone. (2008) dried the stormwater before measuring the PSD and found that 65-99 % of the particles were smaller than 75 μm and only 3% were larger than 250 μm . The pre-treatment could have caused aggregation of the particles.

Measuring the PSD of particulate matter with a Laser Particle Sizer (FRITSCH GmbH, Idar-Oberstein, Germany) using DLS as measuring tech-

nology on stormwater from three different events collected at Albertslund (Denmark) (Nielsen et al. 2015b – paper II), found a similar PSD to the Coulter counter findings (yet unpublished results) (**Figure 7**).

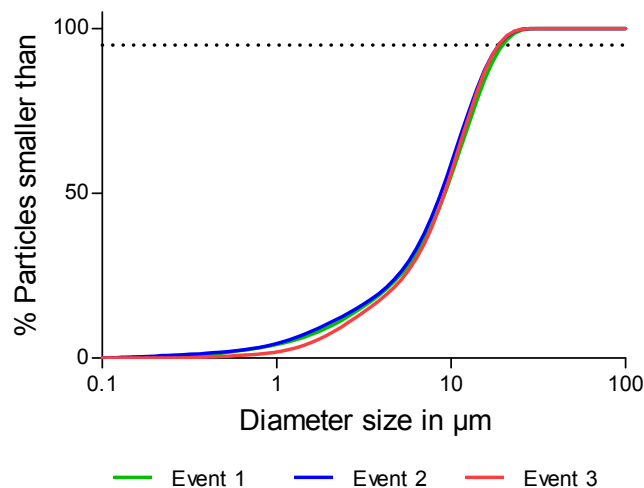


Figure 7: PSD in three stormwater samples from an industrial area in Denmark (Albertslund). The PSD was measured by using DLS (Laser Particle Sizer). (note the logarithmic x-axis). (Nielsen et al. 2015, unpublished analyses).

The particulate matter measured by using DLS showed that 95 % of the particles were $<18 \mu\text{m}$ in diameter. This is a larger average diameter than that observed with the Coulter counter for the same samples but not in the same high size range, as found by Kim et al. (2008). One of the drawbacks of using DLS for stormwater particles is that the reflexive index of the liquid and poly-dispersed index of the particles are required for the analysis, which can be difficult to find when the chemical composition of the particles and liquid is unknown.

3.1.3 Characterising of Colloids and Nano-sized Particles Using DLS

The application of DLS technology on colloids and nano-sized particles in natural samples is infrequent, while the technique is commonly used to measure PSD of industrial nano-sized particles (Abbas et al. 2011; Stone et al. 2010). Nielsen et al. (2015a – paper I) have used DLS to determine the stability in terms of PSD over a 6-month period of nano-sized humic acid (HA-n) colloids and nano-sized iron(III) (Fe-n) nano-particles. The HA-n colloids and Fe-n particles were initially of an unknown size and structure, and the reflexive index and poly-dispersed index were unknown. The PSD of the colloids and nano-particles is shown in **Figure 8**.

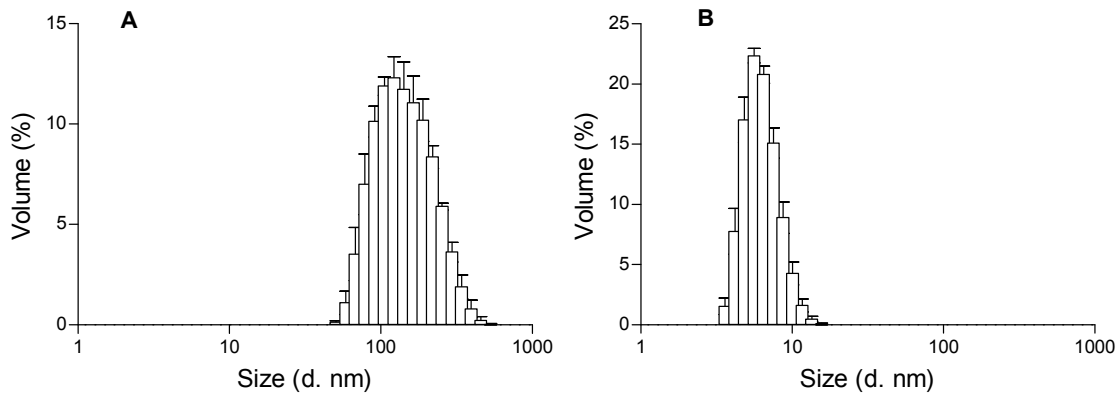


Figure 8: Particle size distribution measured by DLS (Zetasizer) as the hydrodynamic diameter of HA-n colloids (A) and Fe-n particles in suspension (B) at day 0. (note the logarithmic x-axis). (Nielsen et al. 2015a – paper I).

The size of the HA-n colloids was found in hydrodynamic diameter to be 154 ± 4.2 nm over the entire 6-month period. The Fe-n particles were found to increase in size, starting with a hydrodynamic diameter size of 6.4 ± 0.4 nm and ending up with a size of 11 ± 2.2 nm. The PSD was found using a Zetasizer (Malvern Instruments). The PSD for the Fe-n particles was confirmed with TEM, where the crystalline structure of the Fe-n particles was shown together with the perimeter (Nielsen et al. 2015a – paper I). These findings show that the DLS technology can be used on mono-sized-solutions of unknown particles and colloids in aqueous samples.

In Nielsen et al. (2015a – paper I) the HA-n colloid and Fe-n particle are given as relative precise hydrodynamic sizes. This is possible since the suspensions only contain one type of particle or colloid. In stormwater, different sizes, shapes and a mixture of nano-sized particles and colloids will occur, whereby creating a wide range of hydrodynamic sizes. This will yield overlapping sizes and exact hydrodynamic diameters will not be possible to obtain by DLS. The PSD in stormwater has shown the presence of nano-sized particles and colloids in the size range of 5-540 nm in diameter (Nielsen et al. 2015c – paper III; Nielsen et al. 2015e – paper V). The stormwaters from five different European sites did not show any significant difference between one another (Figure 9).

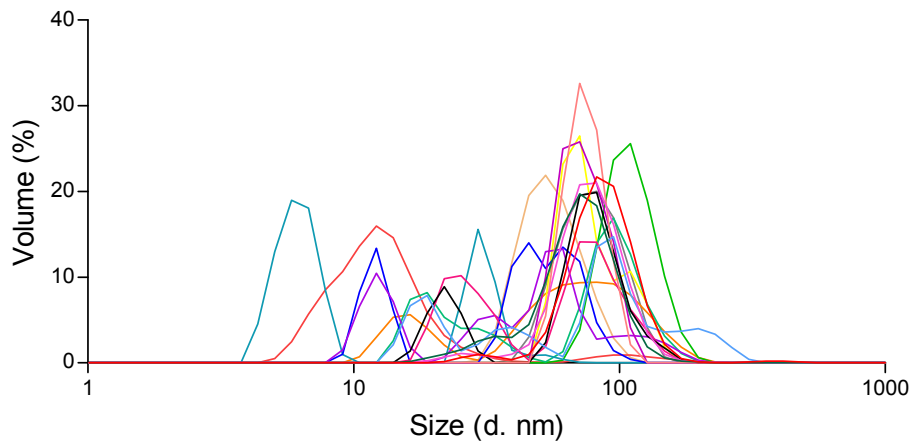


Figure 9: Particle size distribution measured by DLS (Zetasizer) as the hydrodynamic diameter of 18 stormwater samples collected from five different sites around Europe. The sites had catchments of a different character. (note the logarithmic x-axis). (Nielsen et al. 2015b – paper II).

The stormwater contained nano-sized particles and colloids, with most having a PSD within the range of 50-200 nm. That stormwater containing colloids and nano-sized particles has also been shown by Peikertová et al. (2013). They have found particles from car brakes in the size of 200 nm by TEM imaging, and concluded that the nano-sized particles released from the brakes could be released to the aquatic environment, especially since the particles were still found in the water phase after 72 h of sedimentation. TEM images (**Figure 10**), combined with element spectra, show particles from <40 to >300 nm in diameter, consisting of silica, sulphur, iron and titanium (unpublished data). The stormwater originated from the two Swedish sites described in Nielsen et al. (2015e – paper V).

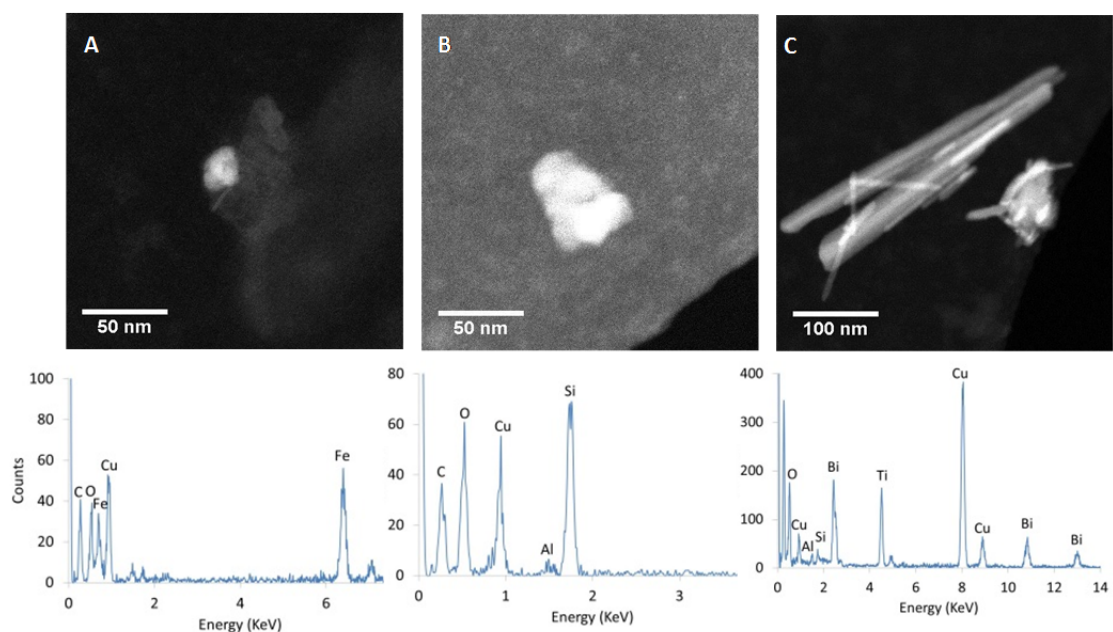


Figure 10: Transmission Electron Microscope (TEM) images of nano-sized particles and colloids in stormwater. The “+” indicates the place where chemical spectra have been measured (a) iron oxide, (b) silica, and (c) titania and bismuth nanowires. Carbon-coated copper TEM grids were used for sample preparation, hence the C and Cu peaks (unpublished data). Dr. Mohammed Baalousha, Assistant Professor at the Center for Environmental NanoScience and Risk, University of South Carolina, USA is acknowledged for his collaboration with these images.

PSD in stormwater with DLS combined with a microscope (NanoSight), found similar distributions to the regular DLS for the colloids and nano-sized particles as by the regular DLS (**Figure 11a**) (unpublished data). By using the microscope during the measurements, Nielsen et al. (2014) found that the scattering light from the stormwater particles was on the limit to be detected. The accordance for the finding of PSD measured on both DLS instruments indicates that colloids occurred in the sample. The white spots in **Figure 11b** show the colloids and nano-sized particles were captured by the microscope. It can be seen that the concentration of particles was low and that the scattering from the particles was low as well.

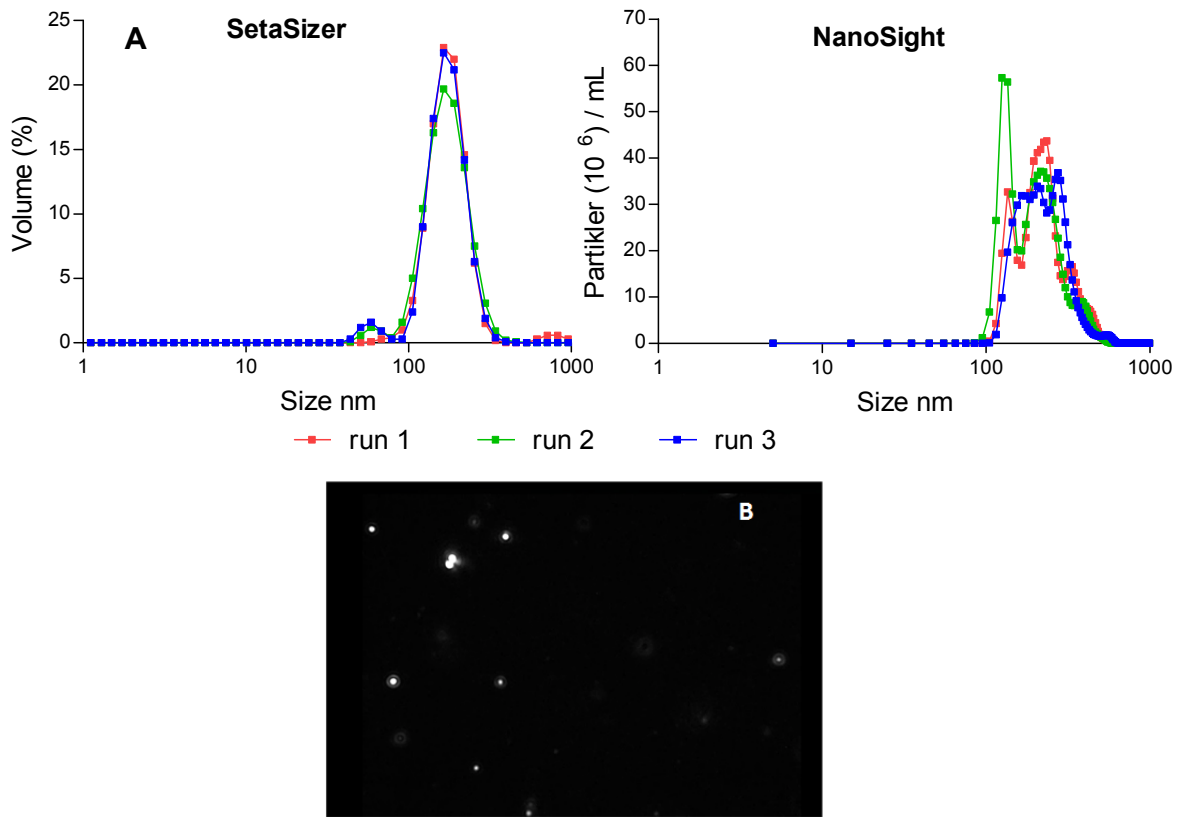


Figure 11: a: Particle Size Distribution of colloids and nano-sized particles in stormwater measured by two different instruments using Dynamic Light Scattering (note the logarithmic x-axis). **b:** a screenshot of the stormwater under a microscope. The white spots are colloids and nano-sized particles scattering light. (Nielsen et al. 2014, unpublished analyses).

3.2 PAHs Associated with Particles, colloids and Nano-sized Particles in Stormwater

Hwang et al. (2006) have studied PAHs in a river receiving stormwater discharges from a 440 km² urban catchment. The study included both TSS and Total Dissolved Solids (TDS), where the difference between the two was that TSS was retained by a 1 µm filter and the filtrate was considered TDS. Sixteen PAHs on the US-EPA surveillance list (ATSDR 1995) were found in the stormwater. Fluoranthene was found in the highest concentration (1.38 µg/L) and acenaphthylene in the lowest concentration (0.002 µg/L) in the TSS samples. No correlation between the concentrations of PAHs and the concentrations of either TSS or TDS was found (Hwang et al. 2006). In stormwater

from a residential area in Denmark where PAHs were measured as the particulate ($>0.7\ \mu\text{m}$) and suspended ($<0.7\ \mu\text{m}$) fractions and yielded an average of 82% (65% - 92%) of the PAHs in the particulate fraction based on five time-proportionally sampled events (Nielsen et al. 2015c – paper III). Herngren et al. (2010) has also measured PAHs in the particulate fractions. They divided the fractions into four:

- $>150\mu\text{m}$ (coarse to fine sand)
- $75\text{-}150\ \mu\text{m}$ (very fine sand to silt)
- $0.45\text{-}75\ \mu\text{m}$ (silt and clay)
- $<0.45\ \mu\text{m}$ (dissolved solid)

Their samples originated from three different catchments: a residential area, an industrial area and a parking lot, and it was shown that all 16 selected PAHs were present in the size fraction containing silt and clay ($0.45\text{-}75\ \mu\text{m}$) from the parking lot. They also showed that the highest concentrations of PAHs were found in stormwater from the parking lot and the industrial area.

Stormwater from two different sites in Gothenburg (Sweden) were analysed for the concentration of PAHs in five different fractions: total, particulate, filtrated, colloidal and dissolved (Nielsen et al. 2015e – paper V). The particulate fraction contained particulate matter retained on a $0.7\ \mu\text{m}$ filter (not measured, but calculated from the total and filtrated concentrations), and the filtrated fraction contained the suspended fraction in the filtrate. The dissolved were extracted on a C_{18} -disk and the colloidal fraction was calculated from the filtrated and dissolved fraction. The percentage distribution of PAHs among the fractions (**Figure 12**) showed that the PAHs were found in fractions, but surprisingly high in the colloidal and dissolved fractions.

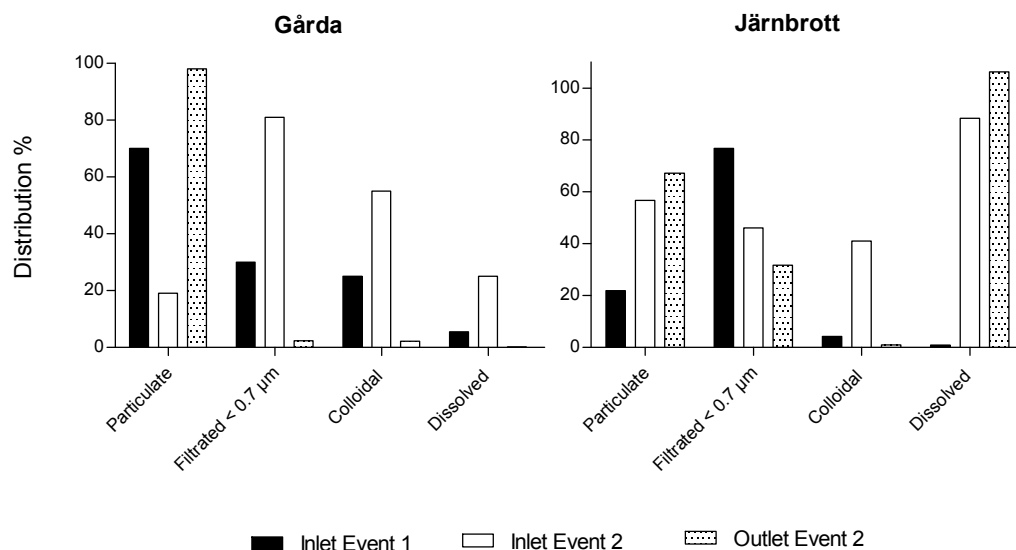


Figure 12: Distribution of PAHs among different fractions from two sites in Gothenburg, Sweden. (Nielsen et al. 2015e – paper V).

During the first event, 70 % of the PAHs at Gårda, but only 22% at Järnbrott, were found in the particulate fraction. The PAHs concentrations in the particulate form may be overestimated as pure water samples and artificial colloidal suspensions showed that as much as 30 – 60% of the PAHs may be sorbed on the surfaces of the 0.7 µm glass-fibre filter. On the other hand, in real stormwater samples, with particles > 0.7 µm, this glass sorption effect is supposed to be much lower because the glass surfaces will rather quickly be covered by particles during filtration. During the second event the filtrated fraction contained the highest PAHs concentration at Gårda, while the dissolved fraction had the highest concentration at Järnbrott. This shows the possibility of PAHs sorbing onto particulate matter, colloids and nano-sized particles, but also to be dissolved in the water. The mechanism for the PAHs being dissolved in water is still unknown, but hypothetically they may form emulsions with other organic contaminants present in the stormwater.

Nielsen et al. (2015e – paper V) also compared the LMW, MMW and HMW PAHs in the fractions and found that the relative composition (REL %) was low for LMW PAHs in all samples, especially in Event 1 (**Figure 13**) at both sites. A long pre-existing dry period (7 days) prior to sampling could have caused a possible volatilisation of the LMW PAHs from the urban surfaces. Relatively high amounts of the HMW PAHs were unexpected found in the dissolved and colloidal fractions

To compare SPE methods for the dissolved fraction containing nano-sized particles, a C₁₈-columns were also used. The extraction procedure was similar to the one for the C₁₈-disk, but extractions were proceeding while following the instructions given by the manufacturer (Sigma-Aldrich 2015). Unfortunately, when loading the 1 L stormwater sample onto the column for extraction, a continuous flow was difficult to achieve. This created drying of the stationary phase, which caused low extraction of the PAHs from the stormwater (data unpublished).

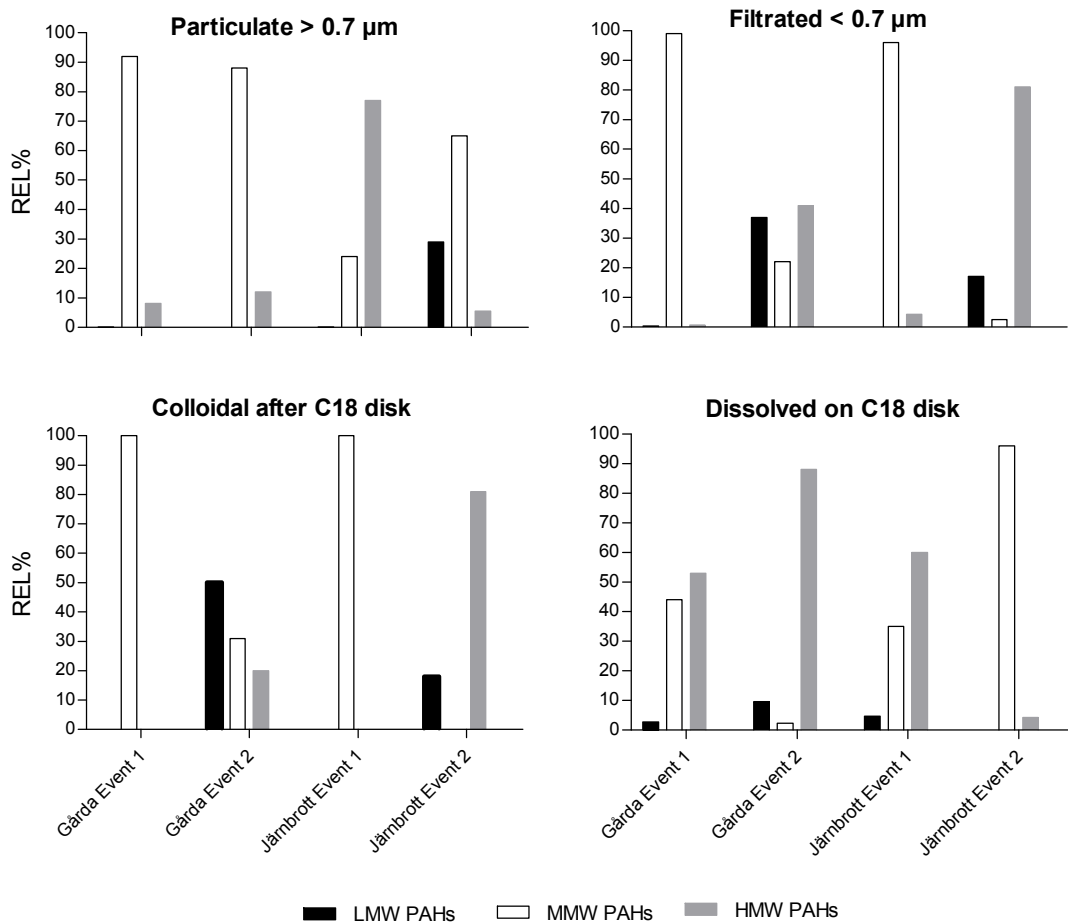


Figure 13: PAHs measured in the fractions (particulate, filtrated, colloidal and dissolved) for samples collected at the two sites in Gothenburg, Sweden. (Nielsen et al. 2015e – paper V)

The LMW PAHs are the most water-soluble and volatile (**Table 6**) of the quantified PAHs, which could explain the low frequency of detection. At both sites, MMW PAHs dominated, and possible sources are rubber tyres and diesel exhausts (Strömvall et al. 2006). The relative loads of HMW PAHs in the particulate fractions were the highest where the highest TSS and smallest

particles (10 – 100 nm) was recorded, i.e. Järnbrott in Event 1 (Nielsen et al. 2015e – paper V). This was explained by the higher Log K_{ow} of the HMW PAHs and their higher ability to sorb to particle surfaces (ATSDR 1995).

3.2.1 Sorption of PAHs to Colloids and Nano-sized Particles

Sorption of PAHs on particulate matter, colloids and nano-sized particles has been evaluated and quantified by controlling the release of PAHs from a silicone membrane into the stormwater (Nielsen et al. 2015d – paper IV). The controlled release of PAHs was quantified after equilibration and was conducted according to the sorption technique “passive dosing” (Birch et al. 2010). The enhanced capacity and free fraction of two PAHs (fluoranthene (Flt) and phenanthrene (Phe)) onto stormwater particulate matter, colloids and nano-sized particles were quantified.

The total concentration of the PAHs measured in the equilibrated solution [$C_{\text{solution(eq)}}$] is the dependent variable, while the concentration measured in equilibrated pure water [$C_{\text{water(eq)}}$] serves as a reference to the freely dissolved concentration in the solution. The free fraction is then determined as the concentration ratio of equilibrated pure water to solution:

$$ff = C_{\text{water(eq)}}/C_{\text{solution(eq)}} \quad (1)$$

The enhanced capacity is then quantified as the concentration ratio between the solution and pure water:

$$E = C_{\text{solution(eq)}}/C_{\text{water(eq)}} \quad (2)$$

$$E = 1/ff \quad (3)$$

An enhanced capacity above 1 indicates that the stormwater is able to contain higher concentrations of PAHs than the reference water (Gouliamou et al. 2012).

The stormwater originated from Albertslund, where low concentrations of PAHs or no detected PAHs were present in the stormwater (Nielsen et al. 2015b – paper II; Birch et al. 2011). Time-proportional samples were collected during four rain events and filtrated through six filter sizes (120 μm , 41 μm , 10 μm , 1.2 μm 0.7 μm and 0.2 μm), giving a total of seven samples, including a total. The filtrates were then applied to the passive dosing technology, where C^{14} labelled Flt and Phe were loaded into the silicone membrane. Equilibrium was reached within 24 h and aliquots were measured on a scintillation counter (Birch et al. 2010). The findings in **Figure 14** showed en-

hanced capacities for two (1 and 4) out of the four events which were higher than 1.

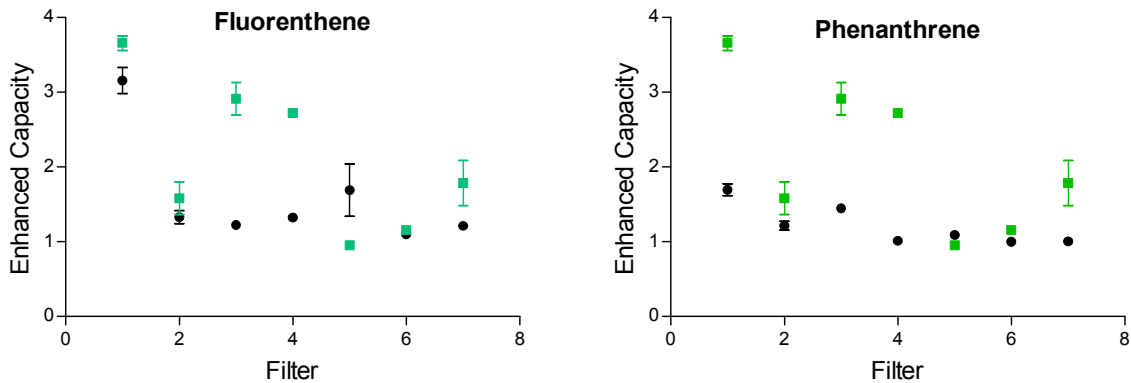


Figure 14: Enhanced capacity measured on stormwater, separated by different filter sizes (1 = total, 2 = 120 µm, 3 = 41 µm, 4 = 10 µm, 5 = 1.2 µm, 6 = 0.7 µm and 7 = 0.2 µm). Black circles = event 1, and green squares = event 4.

The findings by Nielsen et al. (2015d – paper IV) showed that the highest enhanced capacities were found for the total samples (filter 1). Fluoranthene with the highest Log K_{ow} also had the highest enhanced capacity and, therefore, the highest ability to sorb to stormwater particles. The enhanced capacities found for the filtrated stormwater showed a decrease when the particle content was reduced, indicating a loss of sorbing surface for the PAHs. The filtrates containing colloids and nano-particles did not show any evidence of the two PAHs released to the samples. This could be explained by a lack of particles in the catchment which is able to sorb the PAHs, giving the reason why low concentrations of PAHs are found in stormwater from this site (Nielsen et al. 2015b – paper II; Birch et al. 2011).

4 Stormwater Treatment Facilities

As seen in chapters 2 and 3 are pollutants an integrated part of stormwater as metals and PAHs sorbed to the surface of particulate matter, colloids and nano-sized particles. The TSS concentrations representing the particulate matter are in concentrations of 1 – 36,200 mg/L (Table 4, section 2.3). The results are derived from sites receiving stormwater from residential areas, industrial areas, parking lots and highways. Particle size distributions of the particulate matter showed that the majority of the particles were < 10 µm in diameter and colloids and nano-sized particles were also found to be present in stormwater with PSDs of 50 – 200 nm in diameter and with negative surface charges. The PAH concentrations in stormwater were highest for the MMW PAHs and the PAHs were found in the particulate matter fraction, but also found to be associated with colloids and as dissolved.

After implementation of the WFD, the focus on stormwater pollutants has increased to ensure that discharging stormwater to receiving waters is not negatively affecting the ecological and chemical status. The findings, as already seen through chapters 2 and 3 are that stormwater contains pollutants which could have detrimental effects in receiving waters, especially if discharged continuously over a longer period

Treatment and management systems of stormwater are often combined into one common system, where stormwater are retained while it is being treated. For treatment systems it is expected that pollutants will be removed, while management systems control and delay the stormwater discharge into receiving waters. Traditionally, retention ponds have been used to both store and treat stormwater before discharging into receiving waters. **Figure 15** shows three ponds where the one from Albertslund, Denmark and Lyon, France are both detention ponds, made to retain and treat stormwater, while the one at Järnbrott, Sweden only is a treatment pond and not suited to retain large volumes of stormwater. The difference often lies in the way the ponds are constructed, with room for the water level to increase without damaging the nearby area (Persson et al. 1999; Linde et al. 2002; Vollertsen et al. 2006; Hvitved-Jacobsen et al. 2010b).

Stormwater treatments systems made to only treat the stormwater are besides ponds as the one seen in Järnbrott, Sweden (Nielsen et al. 2015e – paper V) often constructed to take up little space such as disc filters. These are treating the stormwater by filtrating particles (size depending on the mesh) from the

stormwater and are not retaining the stormwater over a longer time. Infiltration of stormwater to soil in green gardens is another treatment technique which, in some circumstances can be considered a management technique (Dietz 2007). Green roofs, permeable asphalt and green gardens are management techniques known as Low Impact Development (LID) or LAR in Danish (Lokal Afledning af Regnvand) which remove and sometimes also treats the stormwater in the local area (Linde et al. 2002). This techniques or systems works with infiltration of the stormwater to the soil and thereby removing the stormwater from the stormwater drainage system.

4.1 Ponds

Detention ponds are used to store stormwater and slowly drain it or pump it to receiving waters over a few days. The ponds are characterised by the hydraulic retention time (HRT) for stormwater allowing particles and pollutants to settle, thereby reducing the concentration of pollutants emitted to the aquatic environment. Besides the settling processes treatment of stormwater occurs by microbial degradation, volatilisation, and photolysis as well as plant uptake. The main removal process will be bioaccumulation and sedimentation (Vezzaro et al. 2009).

The layout of the pond, irrespective of whether it is a wet or dry pond, has to be designed to give HRT long enough to reduce the particulate matter and pollutants (**Figure 15**). While wet ponds are designed to remove both particulate matter and dissolved pollutants, the dry ponds are mainly designed to store water for a shorter time and focus on reducing particulate matter. A sand trap, placed before the pond for large particles (>1 mm) to settle, and an oil separator, where oil is removed from the stormwater by phase separation, are often placed in front of the detention pond in Denmark to reduce and create an easy way in which to remove large particles and oil during maintenance (Linde et al. 2002).



Figure 15: Pictures of detention ponds in Europe. Left: detention pond in recreational area in Albertslund, Denmark. Middle: large detention pond in Lyon, France. Right: Järnbrott stormwater pond in a highway area in Gothenburg, Sweden.

4.2 Disc Filters

Disc filters are another treatment technology which was developed with the purpose of removing particulate matter from wastewater (Ljunggren et al. 2005), aquacultures and stormwater (Pedersen 2010). Disc filters can be used in combination with coagulation and flocculation or as the only treatment technique. The disc filters do not retain the stormwater and are therefore considered as a treatment system. In disc filters the stormwater passes through a filter with a chosen mesh size for example 40, 10, 2 μm (Ljunggren et al. 2005; Pedersen 2010; Kruger 2015). Disc filters have been used in wastewater treatment for many years, but have in recent years been tested on stormwater (Pedersen et al. 2010; Nielsen et al. 2015c – paper III).

The disc filter is designed with woven cloth filter elements installed, and uses an inside-out flow pattern; this makes the filter useful for a variety of applications, including tertiary wastewater filtration and stormwater treatment. The water to be treated flows by gravity into the filter from the centre of the drum (**Figure 16**). The stormwater will pass through the filter and particulate matter will be retained on the inside of the filter drum. Once enough solids have accumulated on the inside of the media, the discs are cleaned by a counter-current backwash system (Kruger 2015).

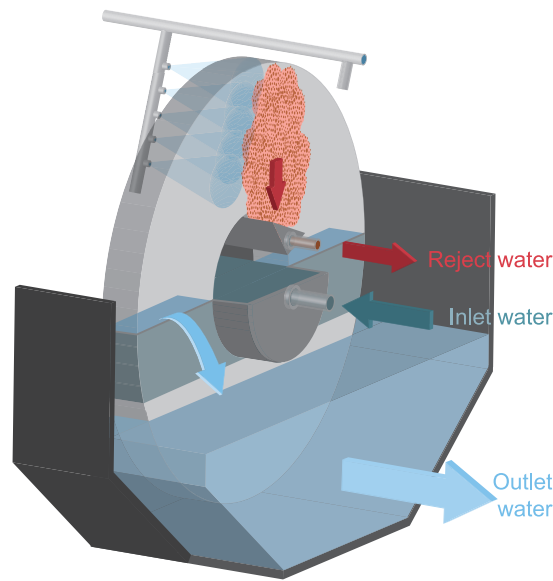


Figure 16: Drawing of the disc placed inside disc filter container. (Nielsen et al. 2015c – paper III).

4.3 Other Treatment Techniques

Some of the less traditional techniques for treating stormwater are the use of permeable surfaces or semi-permeable surfaces. These techniques or treatment systems work by infiltrating stormwater into soil. By using impermeable surfaces on e.g. parking lots, stormwater can be leached directly to the soil and not be collected in the sewage system. Collecting stormwater in ditches by tilting roads and parking lots is another way of redirecting the stormwater away from the sewage system and treating it locally. The ditch could also work as both a channel and a leaching area when heavy rain is falling. Rain gardens are collecting stormwater and from here the stormwater are infiltrated to the soil or taken up by plants. The plants used in rain gardens should be able to live under dry and wet conditions due to dry and flooded periods. For all these techniques and systems sedimentation of particles will appear and should be taking into consideration when placing and designing these LID systems (Linde et al. 2002; wsud-Denmark).

Systems using infiltrating techniques are not common in Denmark, as the drinking water supply is derived from groundwater and a pollutant risk is enhanced. The infiltration techniques are typically designed to operate for 20 years before desilting i.e. mechanical removing of particulate matter. The infiltration systems have traditionally not been designed to remove pollutants,

but rather to reduce the runoff volume of stormwater. Over the last decade, it has been seen that surrounding soils and groundwater have been contaminated if the infiltrated stormwater has not been retained properly (Hatt et al. 2007).

4.4 Removal Efficiencies of Particulate matter, Metals and PAHs in Stormwater Treatment Facilities

The removal efficiencies in detention ponds have been investigated by, e.g. Wu et al. (1998). They quantified TSS, Zn and Fe in three ponds in North Carolina, USA. For two of the ponds, seven rain events were collected; for the last pond, three grab samples were collected. An avg. removal efficiency of 93 % was found for the TSS (**Table 8**). Eighty per cent of the metal Zn was removed, as well as 87 % of the iron.

The removal efficiency between the events varied from 18-100 % for TSS, 22-100 % for Zn and 2-100 for Fe. No explanation for the varying removal efficiencies between the events was given, but as seen in **Table 8** event-to-event variation has also been found by other authors. Nielsen et al. (2015b – paper **II**) that 16-62 % of TSS was removed in a detention pond situated in Albertslund, based on three events during the spring. Another example monitoring campaigns on removal efficiency in a large detention pond, Django Reinhardt Lyon (France), found that 60 – 74 % of Ni, Pb, Cu and Zn were removed. Removal efficiency of PAHs increased with the number of aromatic rings. This was seen by benzo(k)fluoranthene (five rings), which was removed better than acenaphthene (three rings). Their removal efficiency was 67% and 24% respectively (Sebastian et al. 2014). The removal efficiency of pollutants in wet ponds can vary between events, but an effective pond will remove 70-80 % of TSS, 65-75 % of Pb and 45-55 % of Zn (Vollertsen et al. 2006).

Table 8: Removal efficiency on TSS, selected metals and PAHs in the fractions total (t), particulate (p) and colloid (c) fractions in stormwater treatment facilities.

Reference	Treatment facility	Site	Removal efficiency (%)						
			TSS	Ni	Pb	Cu	Zn	Cd	PAHs
Stanly 1996	Detention pond	Greenville, USA (t)	42 - 83	4 - 90	2 - 79	11 - 54	6 - 38	93 - 100	-
Wu et al 1996	Detention pond	N. Carolina, USA (t)	82 - 100	-	-	-	69 - 100	-	-
Birch et al. 2004	Wetland	Sydney, Aus, (t)	9 - 46	12 - 72	27 - 85	21 - 86	33 - 87	-	-
Terzakis et al. 2008	Wetland	Crete, GR (t)	87 - 90	-	20 - 49	31 - 61	26 - 75	-	49 - 71
Sebastian et al. 2014	Detention pond	Lyon, F (t)	53 - 86	32 - 82	41 - 89	6.8 - 88	21 - 84	9 - 81	37 - 65
Nielsen et al. 2015b - paper II	Detention pond	Albertslund (c)	-	<0 - 100	100	41 - 55	34 - 64	-	100
		Albertslund (p)	16 - 62	<0	100	60 - 100	56 - 69	-	100
		Lyon, F (t)	70	41	49	59	41	-	-
Nielsen et al. 2015c - paper III	Disc filter	Bagsværd, DK (c)	-	<0 - 25	<0 - 3.2	<0 - 53	<0 - 78	-	13 - 59
		Bagsværd, DK (p)	5 - 92	59 - 100	100	35 - 100	<0 - 74	-	18 - 86
Nielsen et al. 2015e - paper V	Treatment Pond	Järnbrott, SW (t)	16	35	<0	42	21	-	93
	Settling tanks in serie	Gårda, SW (t)	-125	54	58	71	77	-	<0

- = No data, b<0 = higher concentration in outlet water than in inlet water, TSS = Total Suspended Solid, PAHs = Polycyclic aromatic hydrocarbons, USA = United States of America, F = France, AUS = Australia, GR = Greece, DK = Denmark, SW = Sweden

The removal efficiency of a disc filter was found by Nielsen et al. (2015c – paper **III**). Five to 92 % of the TSS was removed when comparing the inlet to the outlet. The highest removal efficiencies were found when a cationic, non-toxic, starch-based biodegradable organic flocculant was added for flocculation prior to the disc filtration. The same study showed that out of the total concentration of PAHs in the stormwater, 30-40 % were adsorbed to particles < 0.7 µm and were subsequently discharged without any further treatment. Petersen (2010) has tested an identical filter on a similar catchment. She found that up to 64 % of the TSS was removed and that PAHs and metals concentrations were also reduced in the disc filter, and concluded that the removal efficiency of TSS and organic pollutants was sufficient enough to increase the quality of the discharged water.

Removal efficiencies using a filter system treating stormwater in a dual porosity filtration found that 92 - 99 % of the TSS was removed, together with 70 % of Zn and 88 % of Pb. Measurements on organic compounds was not performed, but the TSS and metal removal efficiency was in the same range as seen for the disc filter (Jensen 2009).

The removal efficiency in the stormwater treatment facilities is generally up to 50 % and also higher (**Table 8**). The ponds not only treat the stormwater before discharging into receiving waters, but also manage the stormwater by retaining large volumes. The filters are only working as treatment systems, especially where particulate matter is removed. Higher removal efficiencies could be obtained for all of the treatment facilities by adding flocculants prior to treatment. If the correct flocculant is used, yielding the particles in the stormwater to flocculate or agglomerate, a higher portion of the TSS will be retained. As described for the disc filter used in Nielsen et al. (2015c – paper **III**), the highest removal efficiencies were found when adding an organic cationic flocculent.

4.5 Treatment Effect on Particle Size Distribution

The PSD in stormwater for inlet and outlet stormwater has shown that, irrespective of treatment technology (detention ponds, stormwater pond, disc filter and combined sedimentation tanks), the PSD profile is seemingly unaffected between the inlet and outlet (**Figure 17**).

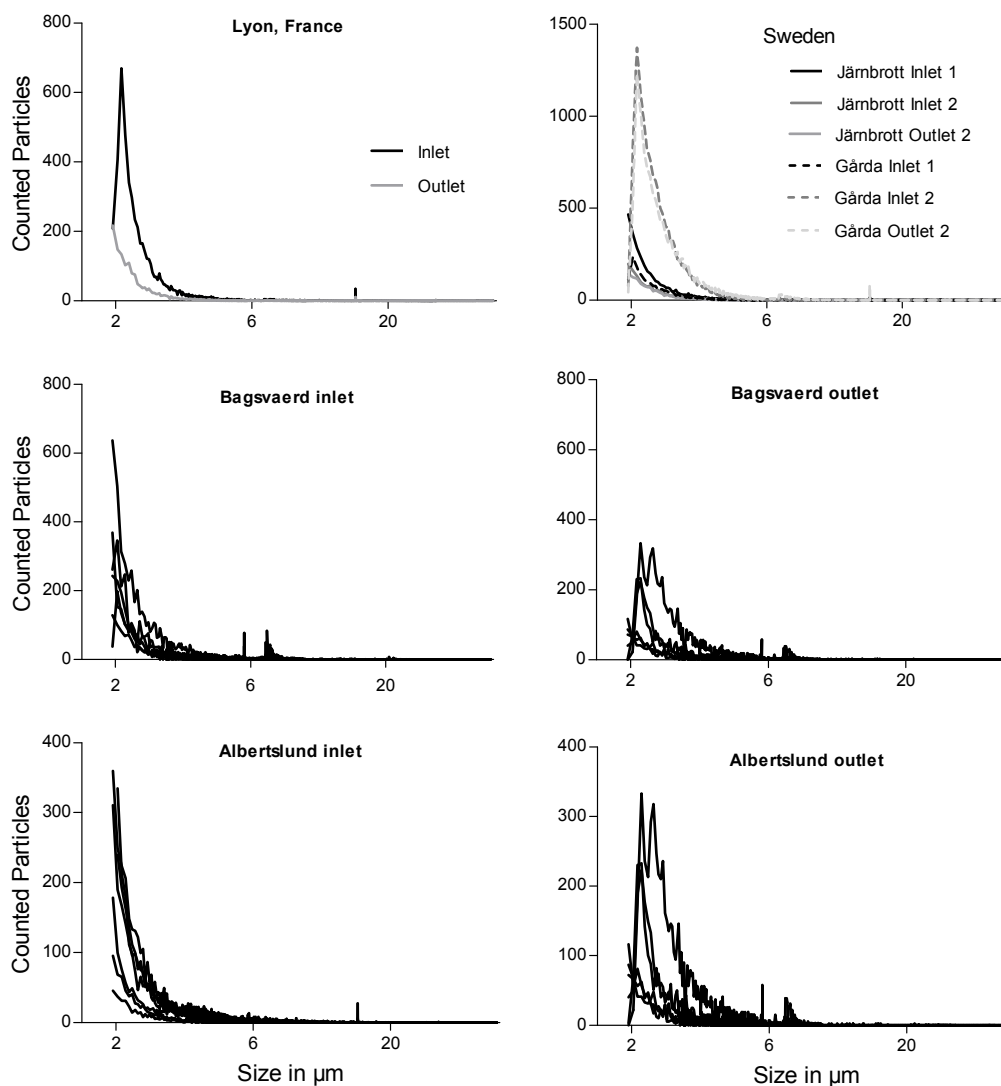


Figure 17: Particle Size Distributions (PSD) based on the Coulter counter principle in stormwater from five European sites (Nielsen et al. 2015b – paper II).

The graphs in **Figure 17** show that the majority of the particles are below 10 μm in diameter. The difference between these graphs and the one shown in **Figure 5** of the PSD measured in Bagsværd and Sweden is that these graphs show the actual particle count on the Coulter counter, while **Figure 5** shows the accumulated particle volume. For all of the sites besides Albertslund, the number of particles was lower at the outlet than at the inlet, but no difference in sizes was seen. This could explain why PAHs were still present in the outlet in the colloidal fraction. As the stormwater treatment technologies only reduce the total number of particles and do not affect the PSD, the same particle surfaces are present in the inlet and outlet, only with a reduced number of particles in the outlet water.

5 Overview and Perspectives

In 2006 Lead and Wilkinson (2006) wrote the following: "Although colloids play a vital role in environmental systems, their precise function is still poorly defined, in spite of decades of research." In 2015 almost 10 years later, a search on Web of ScienceTM of the words "colloids" and "stormwater" gives a mere 31 hits. Where a search on stormwater and nano-particles only gives four hits, only one of the papers describes the PSD of natural stormwater particles (Nielsen et al. 2015c – paper **III**), the other three describe the behaviour of engineered nano-particles in stormwater. Even though the knowledge on the research area has increased, a broader understanding of enhanced transportation of pollutants by colloids and nano-sized particles in stormwater has still not been achieved.

The main issue of characterisation of colloids and nano-sized particles concerns the missing analytical methods. Different PSD techniques can be used to characterise the colloids and nano-sized particles in terms of their size, but these do not tell anything about the chemical content. As try to illustrate in **Figure 18** it can be seen that the lack of analytical methods makes it difficult to answer the research questions, as PSD makes it difficult to describe the chemical composition of the colloids, nano-sized particles and sorbed pollutants. By not knowing the answers to the questions, a full description of what is released from stormwater into receiving waters is not possible.

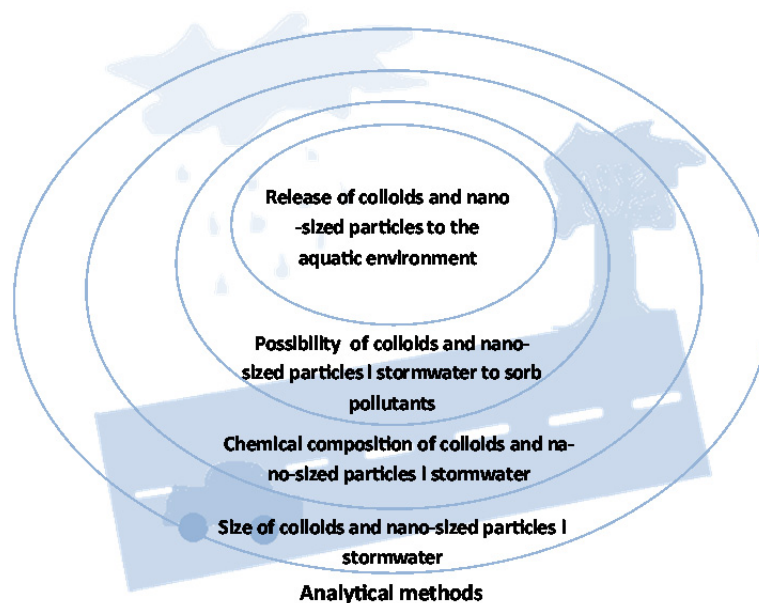


Figure 18: Some of the challenges for investigating the discharge of stormwater into receiving surface waters. The main problem is lack of analytical methods, to determine particle size distribution, chemical content and sorption behavior.

5.1 Particle Size Distribution in Stormwater

Particle size distribution of the particulate matter in stormwater ($>1\ \mu\text{m}$) is described in the literature more than the PSD of colloids and nano-sized particles (Westerlund et al. 2006; Kim & Sansalone 2008; Nielsen et al. 2015b – paper **II**; Nielsen et al. 2015c – paper **III**; Nielsen et al. 2015e – paper **V**). The findings show that particulate matter in stormwater is in the size range of 1-24,500 μm , with the majority of particles $<10\ \mu\text{m}$ in diameter. These findings could explain why pollutants such as metals and PAHs are found in discharged water from stormwater treatment facilities. The PSD of particulate matter in inlet and outlet stormwater has shown similar profiles, despite the stormwater being treated in a detention pond, disc filter or sediment tank (Nielsen et al. 2015b – paper **II**; Nielsen et al. 2015c – paper **III**; Nielsen et al. 2015e – paper **V**). In the literature, it is documented that metals and PAHs are found in discharged stormwater and that the highest concentrations of PAHs are found in the particulate fraction ($>0.7\ \mu\text{m}$); especially the HMW PAHs are found in this fraction (Nielsen et al. 2015c – paper **III**; Nielsen et al. 2015e – paper **V**). Inorganic compounds such as metals have also been found in discharged stormwater from treatment facilities. For a pollutant such as Zn, the highest concentrations (4.6-32 mg/L) were found in the colloidal fractions, while pollutants such as Cd and Co were found neither in the particulate nor colloidal fraction (Nielsen et al. 2015b – paper **II**).

5.2 Terminology

The non-standardised size of the filter mesh used to measure for example, TSS ($2\ \mu\text{m}$ or smaller) (Roesner et al. 2007) creates a difficult comparison of findings. Concentration from a filter with a smaller mesh will be higher than findings with a larger mesh. The separation of organic and inorganic pollutants into different fractions, is described as total, particulate, filtrated, colloidal, suspended, dissolved and truly dissolved throughout the literature (**Figure 19**). Often the particulate fraction area described as what can be retained on a filter with a defined mesh. This filter can change from study to study, but often with the same size as TSS findings. The filtrate from the particulate fraction has been described as the suspended or dissolved fraction.

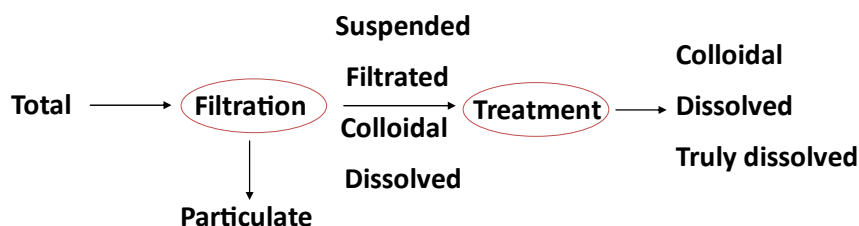


Figure 19: Terminologies used on phase fractions in stormwater literature.

Hwang et al. (2006) and Nielsen et al. (2015c – paper **III**) use the term *suspended*, while Grant et al. (2003), Roesner (2007) and Kim et al. (2009) use the term *dissolved*. Again Nielsen et al. (2015e – paper **V**) use the term *filtrated*. The colloid fraction is often described as the fraction found by separating the suspended fraction from the truly dissolved fraction by C₁₈ SPE or ultra-filtration (Brown et al. 2003; Kalmykova et al. 2013; Kim et al. 2009). Determination of what is in the respective fractions particulate, colloidal and dissolved phase can vary from paper to paper. Therefore, a standardisation of the fractions in the stormwater literature could create a more solid foundation for comparing concentrations of organic and inorganic pollution in the stormwater.

5.3 Legislation

The Environmental Quality Standards for inland surface waters are implemented through the WFD and are used to protect the quality of the aquatic environment. The discharge pollutants described above from stormwater treatment facilities are for some of the metals in the dissolved fraction (<0.45 µm) (As, Cr, Cu, Ni, Pb and Zn), and PAHs as the total fraction (all except for Ace, Acy, BghiP, Flu, Nap and Phe), exceeding the EQS. Since the EQS are not for the discharged water, but for the receiving water, the concentrations will be diluted. The big question is whether the treated stormwater is emitted from the stormwater treatment facility and discharged into surface water. Considering the detention ponds – Basin K, Albertslund (Denmark) and Järnbrott (Gothenburg, Sweden), both of them are part of the natural environment with treated water discharged into a nearby river. They are emitting the treated water into a small river, which ultimately, is discharging into the ocean. If the small river were considered a part of the stormwater treatment facility, the emission would not be under the WFD.

In parallel with the EU Directive, the United States of America have a similar regulation, known as the Clean Water Act, which can be dated back to 1972.

The regulation was made to regulate the discharge of pollutants into surface waters. The regulation allows the U.S. Environmental Protection Agency (US- EPA) to implement pollution control programmes throughout the country. The Clean Water Act requires that all discharge of pollution into surface water must obtain a permit from the National Pollution Discharge Elimination System (NPDES). Besides having clear levels of control to meet the health and environmental objectives, the NPDES is also considering the nature of the receiving water and finding the most cost-effective way in which to control it (Hvitved-Jacobsen et al. 2010a).

The American way of protecting surface waters causes a higher level of control of discharged stormwater, while the European control depends on trust of the government of the individual country.

6 Conclusion

The results of this PhD thesis can be used to conclude the following:

Characterisation of colloids and nano-sized particles in stormwater is a challenge in terms of available analytical methods. In this thesis the DLS technique has been used to characterise the PSD of colloids and nano-sized particles in stormwater. The large variety of particle sizes in the stormwater can affect the characterisation, as large particles can shield smaller particles. Furthermore, the stormwater colloids and nano-sized particles have shown a low reflective scattering, making size measurements difficult as the responses are low. This thesis shows that the DLS technique can be used for stormwater with the mentioned reservations and that colloids and nano-sized particles are present in stormwater. They are in the range of 50 - 200 nm hydrodynamic diameters, with both mono- and poly-dispersed PSD. The majority of the colloids and nano-sized particles found in the stormwater were around 100 nm in diameter. The DLS technique cannot be used to determine sizes of single particle for stormwater colloids and nano-sized particles, and here TEM technique has to be used. The colloids and nano-sized particles in the stormwater challenge the engineering definition of “dissolved fraction” used by authors of existing literature. The dissolved fraction has frequently been described as the fraction which is passed by a $< 0.45 \mu\text{m}$ filter mesh. This thesis show that colloids and nano-sized particles are part of the dissolved fraction and therefore it cannot be classified as “truly” dissolved.

Larger stormwater particles were mainly characterise by the Coulter counter principle, and the majority of the particles present in the total fraction of stormwater had a hydrodynamic diameter of $< 10 \mu\text{m}$. This PSD was found in both inlet and outlet stormwater at different stormwater treatment facilities. The PSD profiles were similar for both inlet and outlet stormwater, and only showing a lower particle concentration at the outlet compared to the inlet. These findings indicate that the particles retained in the stormwater treatment facilities are $> 10 \mu\text{m}$ and those relative large particles are released to receiving waters.

Characterisation in terms of the surface charge of the particles in the stormwater showed that all measured stormwater had a negative surface indicating high content of inorganic particles as clay, silt and organic particles as humic acid or fulvic acid. The zeta potential were quantified in the range of -15 – (-30) mV, ranging from less stable to stable particles. Where the less stable

will be able to flocculate and over time create larger particles which potentially can settle.

Association of pollutants to the particles in stormwater showed that PAHs and metals were present in the all stormwater fractions; large particles, colloids and nano-sized particles. By dividing the stormwater into the fractions of: total, particulate, colloidal and dissolved it was seen that the highest concentration of PAHs was found in the particulate fraction ($> 0.7 \mu\text{m}$). Here MMW and HMW PAHs were in the highest concentrations, measured up to $63 \mu\text{g/L}$ in outlet waters. Even though the highest PAH concentrations were present in the particulate fraction, were still 30 – 40 % of the PAHs present in the colloidal fraction, while for some measurements the dissolved fraction contained up to 80 % of the PAHs. For inorganic compounds Zn quantified in the highest concentration in both the total and suspended fraction of the stormwater. Lead and nickel were present in all of the stormwater, while molybdenum and strontium were below the detection limit in all the stormwater.

The removal of metals in stormwater treatment facilities were found to be up to 78 % of Cr, 66 % of Cu, 96 % of Ni, 61 % of Pb and 74 % of Zn in the particulate fraction, while the suspended fraction showed up to 78 % removal of the metals. Removal efficiencies did not differ between the studied stormwater treatments facilities and none of them where more effective. In general, a lower removal efficiency was found for metals sorbed to the colloidal fraction compared to the particulate fraction.

The PSD did not show a change in the particle range for the particles $< 10 \mu\text{m}$ in diameter during the treatment. Since only a small amount of the $< 10 \mu\text{m}$ particles are removed in the studied stormwater treatment facilities, these particles create an enhanced transportation of the pollutants to receiving waters. The colloidal enhanced transportation of PAHs in the stormwater was also confirmed to be an environmental relevant possibility by evaluation of the partitioning and enhanced capacity of fluoranthene and phenanthrene to stormwater particles, using passive dosing.

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8 Papers

- I. Nielsen K., Mørch-Madsen A., Baun A. and Eriksson E. Characterisation and stability of humic acid and iron nano-sized colloids intended for simulated stormwater experiments (*Submitted*).
- II. Nielsen K., Mikkelsen P. S., Sebastian C. and Eriksson E. Physical and chemical characterisation of stormwater particles (< 50 µm) and associated metals and polycyclic aromatic hydrocarbons (*Manuscript*).
- III. Nielsen K., Mørch-Madsen A., Mikkelsen P. S., Eriksson E. Effect of Disc Filtration with and without Addition of Flocculent on Nano- and Micro-Particles and Their Associated Polycyclic Aromatic Hydrocarbons in Stormwater. *Water*, 2015, 7, 1306–132
- IV. Nielsen K., Mayer P., Eriksson E. Co-transport of PAHs by Particulate Matter, Colloids and Nano-sized Particles - using Analytical Passive Dosing to Determine the Enhanced Capacity of Stormwater (*Manuscript*).
- V. Nielsen K., Kalmykova Y., Strömvall A-M., Baun A., Eriksson E. Particle Phase Distribution of Polycyclic Aromatic Hydrocarbons in Stormwater – Using Humic Acid and Iron Nano-sized Colloids as Test Particles. *Science of the Total Environment*, 2015, 532, 103–111

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The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four sections:

Water Resources Engineering, Urban Water Engineering,
Residual Resource Engineering and Environmental Chemistry & Microbiology.

The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

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